Supporting Information

Toward a Comprehensive Global Emission Inventory of C_4–C_{10} Perfluoroalkanesulfonic Acids (PFSAs) and Related Precursors: Focus on the Life Cycle of C_8-Based Products and Ongoing Industrial Transition

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S1 Nomenclature

S1.1. Terminology regarding chemicals

This study focuses on the global emissions inventory of perfluoroalkanesulfonic acids (PFSAs) and their precursors from the life cycle of perfluorooctanesulfonyl fluoride (POSF)-based products. POSF is one of the perfluoroalkanesulfonyl fluorides (PASFs) (see Table S1), and PASF-based compounds are a large group of chemicals containing at least one "$C_nF_{2n+1}SO_2$—" moiety[1] and can be divided into two groups: non-polymers and polymers. Major non-polymeric compounds are listed in Table S1. The polymeric compounds are so-called "side-chain fluorinated polymers" consisting of variable compositions of non-fluorinated carbon backbones with PASF-derivatives (such as perfluorooctanesulfonamidoethyl acrylate) on side chains. Non-polymeric and polymeric PASF-based compounds are potential precursors of PFSAs such as perfluorooctanesulfonic acid (PFOS).

Depending on the availability of information (structure, CAS number, trade name, etc.), we named all substances involved in this *Supporting Information* and the main text in three ways:

(i) The majority have a known structure and terminology, and these are named according to the number of carbons on the alkyl chain and the functional group, e.g. the compound with four fluorinated carbons and a sulfonate group is named perfluorobutane sulfonic acid (PFBS);

(ii) Those that have a known structure and/or CAS number but no terminology proposed yet are named after their registered CAS number (in the form of CAS No. *xxx-xx-x*);

(iii) For the few compounds that have a trade name but an unknown structure, terminology and CAS number, they are named after their trade name (e.g. in the form of FC *xxx*).

Table S1: The acronym, name or structure, and CAS number of some of the major non-polymers investigated.

Acronym 1	Acronym 2	Name / Structure	CAS number
Perfluoroalkanesulfonyl fluorides (PASFs)			
C_4 PASF	PBSF	$C_4F_9SO_2F$	375-72-4
C_5 PASF	PPeSF	$C_5F_{11}SO_2F$	375-81-5
C_6 PASF	PHxSF	$C_6F_{13}SO_2F$	423-50-7
C_7 PASF	PHpSF	$C_7F_{15}SO_2F$	335-71-7
C_8 PASF	POSF	$C_8F_{17}SO_2F$	307-35-7
C_9 PASF	PNSF	$C_9F_{19}SO_2F$	68259-06-3
C_{10} PASF	PDSF	$C_{10}F_{21}SO_2F$	307-51-7
Perfluoroalkanesulfonic acids (PFSAs) & their major derivatives			
PFBS	C_4 PFSA	$C_4F_9SO_3H$	375-73-5
K-PFBS	-	$K^+ C_4F_9SO_3^-$	29420-49-3
PFHxS	C_6 PFSA	$C_6F_{13}SO_3H$	355-46-4
K-PFHxS	-	$K^+ C_6F_{13}SO_3^-$	3871-99-6
PFOS	C_8 PFSA	$C_8F_{17}SO_3H$	1763-23-1
NH$_4$-PFOS	-	$NH_4^+ C_8F_{17}SO_3^-$	29081-56-9
K-PFOS	-	$K^+ C_8F_{17}SO_3^-$	2795-39-3
NEt$_4$-PFOS	-	$N(C_2H_5)_4^+ C_8F_{17}SO_3^-$	56773-42-3
PFDS	C_{10} PFSA	$C_{10}F_{21}SO_3H$	335-77-3
NH$_4$-PFDS	-	$NH_4^+ C_{10}F_{21}SO_3^-$	67906-42-7
Perfluorooctanesulfonamides/-sulfonamido ethanols (xFOSA/Es)			
FOSA	-	$C_8F_{17}SO_2NH_2$	754-91-6
MeFOSA	-	$C_8F_{17}SO_2NH(CH_3)$	31506-32-8
EtFOSA	Sulfluramid	$C_8F_{17}SO_2NH(C_2H_5)$	4151-50-2

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FOSE	-	$C_8F_{17}SO_2NHCH_2CH_2OH$	10116-92-4
MeFOSE	-	$C_8F_{17}SO_2N(CH_3)CH_2CH_2OH$	24448-09-7
EtFOSE	-	$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OH$	1691-99-2

Other perfluoroalkanesulfonamides (xFASAs)

FBSA	-	$C_4F_9SO_2NH_2$	30334-69-1
FPeSA	-	$C_5F_{11}SO_2NH_2$	82765-76-2
FHxSA	-	$C_6F_{13}SO_2NH_2$	41997-13-1
FHpSA	-	$C_7F_{15}SO_2NH_2$	82765-77-3
MeFBSA	-	$C_4F_9SO_2NH(CH_3)$	68298-12-4
MeFPeSA	-	$C_5F_{11}SO_2NH(CH_3)$	68298-13-5
MeFHxSA	-	$C_6F_{13}SO_2NH(CH_3)$	68259-15-4
MeFHpSA	-	$C_7F_{15}SO_2NH(CH_3)$	68259-14-3
EtFBSA	-	$C_4F_9SO_2NH(C_2H_5)$	40630-67-9
EtFPeSA	-	$C_5F_{11}SO_2NH(C_2H_5)$	162682-16-8
EtFHxSA	-	$C_6F_{13}SO_2NH(C_2H_5)$	87988-56-5
EtFHpSA	-	$C_7F_{15}SO_2NH(C_2H_5)$	68957-62-0

Other perfluoroalkanesulfonamido ethanols (xFASEs)

FBSE	-	$C_4F_9SO_2NHCH_2CH_2OH$	34454-99-4
FPeSE	-	$C_5F_{11}SO_2NHCH_2CH_2OH$	N.A.
FHxSE	-	$C_6F_{13}SO_2NHCH_2CH_2OH$	106443-63-4
FHpSE	-	$C_7F_{15}SO_2NHCH_2CH_2OH$	167398-54-1
MeFBSE	-	$C_4F_9SO_2N(CH_3)CH_2CH_2OH$	34454-97-2
MeFPeSE	-	$C_5F_{11}SO_2N(CH_3)CH_2CH_2OH$	68555-74-8
MeFHxSE	-	$C_6F_{13}SO_2N(CH_3)CH_2CH_2OH$	68555-75-9
MeFHpSE	-	$C_7F_{15}SO_2N(CH_3)CH_2CH_2OH$	68555-76-0
EtFBSE	-	$C_4F_9SO_2N(C_2H_5)CH_2CH_2OH$	34449-89-3
EtFPeSE	-	$C_5F_{11}SO_2N(C_2H_5)CH_2CH_2OH$	68555-72-6
EtFHxSE	-	$C_6F_{13}SO_2N(C_2H_5)CH_2CH_2OH$	34455-03-3
EtFHpSE	-	$C_7F_{15}SO_2N(C_2H_5)CH_2CH_2OH$	68555-73-7

N-Methyl perfluoroalkanesulfonamido ethyl acrylates (MeFBSEAs)

MeFBSEA	-	$C_4F_9SO_2N(CH_3)CH_2CH_2OC(O)CH=CH_2$	67584-55-8
MeFPeSEA	-	$C_5F_{11}SO_2N(CH_3)CH_2CH_2OC(O)CH=CH_2$	67584-56-9
MeFHxSEA	-	$C_6F_{13}SO_2N(CH_3)CH_2CH_2OC(O)CH=CH_2$	67584-57-0
MeFHpSEA	-	$C_7F_{15}SO_2N(CH_3)CH_2CH_2OC(O)CH=CH_2$	68084-62-8
MeFOSEA	-	$C_8F_{17}SO_2N(CH_3)CH_2CH_2OC(O)CH=CH_2$	25268-77-3

S1.2. Terminology regarding product life cycle

This emission inventory is estimated by investigating the fate of certain compounds during the life cycle (production, use and disposal phases; see Figure S1) of relevant products that contain PFOS and their precursors as active ingredients, unreacted or partially reacted raw materials or intermediates (residuals) or byproducts (impurities). We use the major active ingredients in the products to name product types, and we assign an average duration for each step in the product life cycle (steps shown in Figure S1). The duration of the use phase is also called the product lifetime.

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Life-cycle of products

Figure S1: Scheme of the product life cycle.
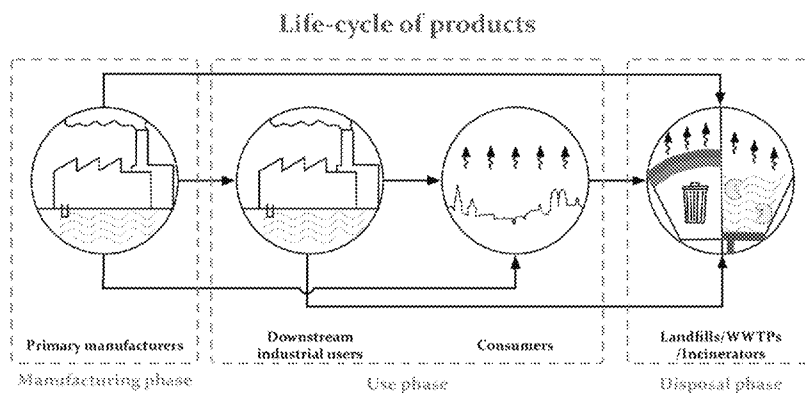
S1.3. Terminology regarding geographical distribution and units

In some cases, we divided the global emissions into two country groups according to the similarity of production history. Country group I (CGI) comprises initial producing countries such as Japan, Western Europe and the United States (US), while emissions for China and Brazil are reported separately. All units including abbreviations are documented according to the International System of Units (SI), e.g., "t" represents a metric ton or tonne.

S2. Methodologies of detailed emission estimates of each individual source

In this study, we followed the methodology developed to estimate the global emission inventory of perfluoroalkylcarboxylic acids (PFCAs) by Wang et al.[2], but with refinements that are specifically made for PFSAs. In this section, we list detailed information, estimations and assumptions used for the quantification of emissions from each source, so that our emission inventory can be further developed and refined in the future when more information becomes available. In Table S23 at the end of this document, we provide for all parameters their origin (estimated or assumed), estimated uncertainty level, and location of relevant details in this document. Figure S2 below shows the general claculation steps and inputs used to calaculate emissions across the production and use and disposal phases.

Figure S2. Flowchart of quantification steps across the life cycle in the present study for a) emissions of PFSAs and b) emissions of PFSA precursors.
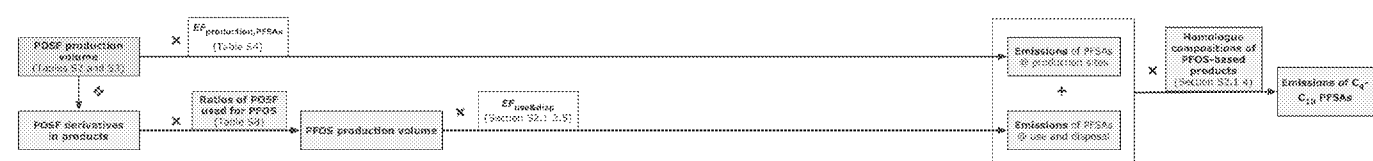
S2.1. Emissions from POSF-based products

POSF-based products are a large family of chemicals that are derivatives of the parent compound perfluorooctanesulfonyl fluoride (POSF), which has been manufactured through electrochemical fluorination since 1958. The production of POSF-based products can be divided into three periods: In the first period (1958–2002), the majority of products were produced in country group I (Japan, Western Europe and the US) with some minor production in China. 3M was the first and largest manufacturer with three sites in the US (since 1958) and one site in Belgium (since 1971).[3,4] Miteni (formerly Rimar) in Italy, Dianippon Inc. in Japan, and Changjiang Chemical Plant in China (since the late 1970s) have also produced POSF-based products.[4,5] A few other companies (e.g. Air Products, BASF, Bayer, Borax Research, Ciba-Geigy, GIPKh (Russia), Tohoku Hiryo, Tokuyama Soda, and Yarsley Research) were also active in ECF;[5–8] however, no information is available yet to confirm or to quantify the production of POSF-based products by these companies. In the second period (2003–2015), produced in country group I ceased their production one after another, while manufacturers in China[9] started large-scale production with a major use as insecticide in Brazil.[10] In the third period (2016–2030), two scenarios are applied to China and Brazil. As a lower scenario, it is assumed that these producers reduce their production quickly in response to global regulatory efforts. China is assumed to linearly phase-out production by 2018 and Brazil to cease production of insecticide after 2015. While as a higher scenario, China is assumed to require more time to linearly phase out production (by 2025) (see Table S2), and Brazil is assumed to maintain a constant production level of insecticide through 2030 (see Table S10).

POSF-based products include diverse polymers and non-polymers in highly diverse industrial and consumer applications (see Figure S3), where only non-polymers may readily degrade to PFOS. An additional complexity is that PFOS is present as an impurity in POSF-based products that can be released during the product life cycle. Moreover, POSF-based products are a mixture containing a majority of C_8-based components (including residuals) and a small amount of their lower and higher homologues that can degrade to different PFSA homologues. In order to deal with these complexities and establish a global emission inventory of PFSA homologues and their precursors, we re-assessed earlier reviews[11–15], considered a large number of recently published documents (references discussed and provided throughout this document), and applied a stepwise approach to assessing PFSA emissions from the life cycle of POSF-based products.

MeFOSA — 100% — on-site
- 82-87% ♣ Fluorochemical Urethane
- 13-18% ♣ polymer melt additive for nonwoven substrates

EtFOSA — 59% — on-site
- 75-80% ♦ FC171 (68958-61-2), polymeric, surfactant
- 19±2% ♦ active ingredient for insect control
- 2±0.5% ♦ surfactant for the wetting of protective coatings
- <1% ♦ surfactant for oil well industries
- <1% ♦ surfactant for mining industries
- <1% ♦ wetting agent for thickeners (Carbopol)
- <1% ♦ aid for the gelling of medical waste solutions

MeFOSE — >98% — on-site
- 35-40% ♣ Fluorochemical Adipate
- 1-5% ♣ Fluorochemical Urethane
- 1-5% ♣ Fluorochemical Esters
- <1% ♣ Fluorochemical Esters

MeFOSEA (25268-77-3) — >99% — on-site
- 90-95% ♣ Fluorochemical Acrylates
- 3-8% ♥ Fluorochemical Acrylates (92265-81-1)

MeFOSEMA (14650-24-9) — (♣) Fluorinated polymers

FX12, EtFOSE — >99.5% — on-site
- 5-10% (♣) Fluorochemical Allophanate
- 5-10% (♣) Fluorochemical Urethanes
- <1% (♣) Fluorochemical Esters
- 75-80% ♥ FC 807 (30381-98-7), paper packaging
- 1-3% ♦ FC 170C, C8F17SO2N(C2H5)(CH2CH2O)xCH3, surfactant

EtFOSEA (FX13, 423-82-5) — 0% — on-site — 100% Fluorinated polymers **
EtFOSEMA (FX14, 376-14-7) — 100% — on-site
- 19% Fluoromethacrylate oxide **
- 17% Fluoroaliphatic polymericesters **
- 12% Fluorinated alkyl ester **
- 60% Fluorinated alkyl acrylate **
- <1% Fluorinated alkyl methacrylate **

17809-69-4 — ♦ used as foamer in AFFF
38006-74-5 — ♦ surfactants for the mining and oil well industries
PFOSSA — ♦ surfactant in cleaners, floor polishes, consumer denture cleaner
MeFOSSA — ♣ consumer carpet protectors, likely polymeric
♣/♦ POSF is used as intermediate for upholstery and carpet protectors and cleaners
♦ POSF is used as a reactive intermediate in the synthesis of a foamer for use in AFFF — including ≤ 5.5 % POSF were used to make PFOS and its salts as ♦
Others
FOSA — byproduct during production of Me- & Et-FOSA, present ≤ 0.1% in various POSF-based products and 0.01% in indirect food additive products

3M POSF in 1997 in US
- 90% on-site
- 10% off-site — <100% exported

Percentages at left (parent yields):
- <1.1% (1.3%) MeFOSA
- <1.1% (0.8%) EtFOSA
- 40% (43.7%) MeFOSE
- 50-55% (38%) MeFOSEA
- 1-5% (1.7%) MeFOSEMA
- 53% (51.4%) FX12, EtFOSE
- <2-6% (0.3%) EtFOSEA
- <1% (1.5%) EtFOSEMA
- <1.1% 17809-69-4
- <1.1% 38006-74-5
- <0.6% (0.3%) PFOSSA
- <1.1% MeFOSSA
- 2.2 %
- <1.1%
- 0.01 - 0.1% FOSA

Legend:
♣ Aftermarket/Consumer Products
♣ Apparel/Carpet/Textiles Products
♥ Paper and Packaging Products
♦ Performance Chemical Products
(♣) likely Apparel/Carpet/Textiles Products

polymeric products
non-polymeric products
undefined products

Source: SciFinder©, AR226-0576 to AR226-0585, AR226-0600, AR226-0681, AR226-0928

* The percentages in this figure represent the relative yields of each product from its parent compound. The numbers in brackets are derived from the AR226-0600, while the others are taken from AR226-0576 to AR226-0585 and AR226-0681. It is unknown in which form or end products the chemicals were distributed off-site. In order to simplify the calculations, it is assumed that both on-site and off-site chemicals share the same use pattern as described in this figure.
** These chemicals are used as intermediates to produce surfactants, textile treating resins or paper sizings. The exact end use of each species is not yet determined.

Figure S3: Substance flow of POSF-based products manufactured by 3M in 1997 in the US.

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In this approach (see Step 1 of Figure 1 in the main publication), we divided the product life cycle of POSF-based products into two phases based on data availability: (i) production and (ii) use and disposal. Note that our estimates are normalized to "POSF-equivalents" ($C_8F_{17}SO_2F$) based on the POSF moiety ($C_8F_{17}SO_2$) in POSF-based products so as to consistently combine data from different sources. In addition, we use "xFOSA/Es" (perfluorooctanesulfonamides/sulfonamido ethanols) as a surrogate of direct PFSA precursors that can partially degrade into PFSAs in the environment and biota.

We first focus on emissions that occurred at primary production sites where POSF-based chemicals have been produced based on several industrial documents regarding (i) production volumes of several POSF-based chemicals and (ii) mass flow at three production sites (see section S2.1.2). In the mass flow studies, flows into environmental media (air, water and soil) were reported.

Second, we focus on emissions that occurred during product use and disposal by the downstream industrial users and end consumers (see section S2.1.3). These include (i) direct emissions of PFSAs that are active ingredients and impurities in products and (ii) direct emissions of non-polymeric PFSA precursors that are unreacted residuals in both polymeric and non-polymeric products. It should be noted that our estimates describe the generic fate of grouped POSF-based products (i.e. polymers and non-polymers), since it is neither practical nor realistic to attempt to assess the release and fate of each individual species during the use and disposal phase. We do, however, complete a scenario analysis to assess the range of waste stocks potentially generated as well as the potential formation of PFOS precursors from the degradation of polymers in these wastes.

We then focus on indirect emissions of PFSAs from the degradation of non-polymeric POSF-based species released into the environment as based on laboratory degradation studies (see Section S2.1.3.7). This degradation is calculated using the CliMoChem multimedia environmental fate model, which is introduced and described further in section S3.

In the final step, all estimates are broken down on a homologue basis based on available information on the relevant homologue compositions of POSF-based products (see section S2.1.4).

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S2.1.1. Production volumes of POSF

The production volumes of the parent compound, POSF, were estimated mainly based on industrial survey results (see Table S2 & Table S3).

Table S2: Estimated 3M, global (excluding China), and Chinese POSF production volumes in 1958–2002 in tonnes.

Year	3M [t]	Global [t]	Year	3M[t]	Global [t]	Year	3M [t]	Global [t]	China [t]
1958	21	26	1973	339	423	1988	1905	2381	0
1959	42	53	1974	360	450	1989	1905	2381	0.5
1960	64	79	1975	381	476	1990	2177	2722	0.75
1961	85	106	1976	533	667	1991	2177	2722	1
1962	106	132	1977	686	857	1992	2177	2722	1.25
1963	127	159	1978	838	1048	1993	2177	2722	1.5
1964	148	185	1979	991	1238	1994	2177	2722	1.75
1965	169	212	1980	1143	1429	1995	2903	3629	2
1966	191	238	1981	1295	1619	1996	2903	3629	2.25
1967	212	265	1982	1448	1810	1997	2903	3629	2.5
1968	233	291	1983	1600	2000	1998	2903	3629	2.75
1969	254	318	1984	1753	2191	1999	2903	3629	3
1970	275	344	1985	1905	2381	2000	3494	4368	3
1971	296	370	1986	1905	2381	2001	175	218	3
1972	318	397	1987	1905	2381	2002	121	151	30

Table S3: Estimated POSF production volumes between 2003 and 2015 in country group 1 (CG 1, including Japan, Western Europe and the US) and China in tonnes.

	CG I [t]		China [t]
Year	lower	higher	
2003	50	160	50
2004	50	160	100
2005	73	162	170
2006	50	100	250
2007	25	50	250
2008	0	0	250
2009	0	0	130
2010	0	0	100
2011	0	0	130
2012	0	0	130
2013	0	0	150
2014	0	0	170
2015	0	0	170

1958–2002: The estimates of production volumes were based on 3M's POSF production history reported to the Stockholm Convention.[16] Following Armitage et al.,[13] it was assumed that production increased linearly from zero to one fifth of 1985-1989 production levels between 1957 and 1975 and that production increased linearly between 1975 and 1985. Our total estimated production value for the period 1957 to 1975 is slightly higher than the value published by Armitage et al.[13], and the source of this difference is unclear. POSF production in China is reported to have started on a very small scale in the 1970s with very limited production and use,[17] and it started to increase in the early 1990s and reached a reported production of circa. 3 t/yr in 1997 or 1998.[18] Therefore, we assumed a linear increase in production from 0.5 t/yr in

1989 to 3 t/yr in 1999 and that it remained at 3 t/yr before rising to 30 t/yr in 2002, when larger scale production started.

2003–2015: After 3M ceased its global production in 2002, there were still a few producers in country group I producing POSF-based products: About 50–160 tonnes were produced in 2003 in Belgium, Germany, Italy and Japan;[19] and 73–162 tonnes were produced in 2005.[20] We assumed that the production in country group I decreased linearly thereafter and only negligible amounts were produced after 2008 due to regulatory efforts, such as being regulated under the EU Directive 2006/122/EC and the Stockholm Convention Annex B. During this same period, large-scale production began in China in 2003. Reported annual production before 2004 was less than 50 t/yr, expanded to about 250 t/yr in 2006 and 2008, declined to 130 t/yr in 2009 and 100 t/yr in 2010.[5,9,17,21,22] Production values in 2015 were estimated at 170 t/yr.[23]

2016-2030: For China, we assumed that the 2015 level of production (i) linearly decreased and reached a negligible level by 2018 (lower scenario) and (ii) linearly decreased and reached a negligible level by 2025 (higher scenario). This is based on China's ratification of Amendments to Annexes A, B and C of the Stockholm Convention specifying that from March 26, 2014 efforts should be made to develop substitutes for current exempted uses of PFOS and POSF as soon as possible and before the exemptions expire, and to gradually eliminate their production and use.[24] The national project co-financed by the Global Environment Facility has also been approved for implementation to support the reduction and phase-out of ongoing uses of PFOS in China between 2017 and 2021.[25] No production is assumed to exist during this period for CGI.

S2.1.2. Releases of non-polymeric POSF-based compounds from production sites

There are more than 600 intermediate steps associated with the production of POSF-based compounds, and each step may release POSF-based species into the environment. We assumed emission factors at all production sites to be identical and remain the same over entire periods. Based on information about the chemical compositions of waste streams, physicochemical properties of these chemicals, and industry emission reduction measures, we estimated emission factors of POSF, PFOS and xFOSE/As during two time periods (1958–1997 and 1998–2030) (see Table S4). We used xFOSE/As as a surrogate for direct PFSA precursors including xFOSAs, xFOSEs, and xFOSE(M)As. Other potential precursors were likely released from production sites as well, but they were not monitored, and thus, cannot be included here.

Table S4: Estimated emission factors of POSF, PFOS and xFOSA/Es being released from production sites between 1958 and 2030, in % of the total annual production mass.

		Release to			Total
		air	water	land treatment	
1958-1997	POSF	0.81%	0.0%	0.6%	1.4%
	PFOS	0.0%	0.54%	1.0%	1.5%
	xFOSA/Es	0.004%	0.06%	1.1%	1.1%
1998-2030	POSF	0.20%	0.0%	0.0%	0.2%
	PFOS	0.0%	0.27%	0.0%	0.3%
	xFOSA/Es	0.001%	0.03%	0.0%	0.0%

1958–1997: In the US, 3M produced POSF-based products mainly at their facility in Decatur, AL with some minor production in Cottage Grove, MN (pilot plant production only) and Cordova, IL (ceased before 1997).[26,27] Based on the targeted monitoring conducted in 1997–1999 and the production data for 1997–1999, 3M reported that about 4% of the non-polymeric POSF-based compounds produced in the Decatur

facility entered the environment, either through direct release to air and natural waters after waste treatment processes or through land treatment (normally for agriculture) via POSF-based products contained in activated sludge (see Table S5). The reported emission levels to water in Table S5 were derived from the measurements conducted after a carbon adsorption treatment was installed in 1998, which reduced possible release to natural waters by 50%. Thus, we doubled our estimates accordingly to represent the emissions to water in the time before 1998. Additionally, there were also some minor releases of PFOS to water from the Cottage Grove facility. It should be noted that in 3M's report, the actual amount of solid wastes generated from the Decatur facility in 1997 was estimated to be about 490 tonnes (about 70% incinerated and 30% landfilled in a hazardous waste landfill), which is much higher than the 37 tonnes we used for our estimates.[28] However, 3M's estimates were likely derived from the total fluorine content,[27] and therefore includes not only all polymeric and non-polymeric POSF-based wastes, but also other fluorinated by-products. Consequently, we could not use this estimate in our calculations.

1998–2015: In 1998, a carbon adsorption treatment system was installed as part of the wastewater treatment process at the Decatur facility. It reduced releases from the wastewater treatment system by 40% to air and by 50% to natural waters in 1998 compared to the levels in 1997.[28] In 1999, the release to air was further reduced to about 25% of the level in 1997,[27] which we used to represent the emission level to air for the whole period. In addition, sludge from the Decatur facility started to be transported to an offsite landfill instead of being used for land treatment.[28] Hence, we adjusted the factors accordingly (see Table S4).

Table S5: Reported exposure information profile from 3M's production sites in the US, in tonnes. All data were normalized to "POSF-equivalents" and combined with the POSF production volume of 1850 t in the US in 1997.[29] N.Q. = not quantified; N.A. = not available; xFOSA = x-perfluorooctanesulfonamide; xFOSE = x-perfluorooctylsulfonamido ethanol; xFOSE(M)A = x-perfluorooctanesulfonamidoethyl (methyl)acrylate.

Site	Chemical	Releases [t] to			Solid waste *** [t]	Reference
		Air	Water *	Land treatment **		
Cottage Grove	PFOS	N.Q.	0.5	0.0	3.4	30
Decatur	POSF	15.0	0.0	11.8	N.Q.	27
	FOSA	N.Q.	0.2	0.0	N.Q.	31
	PFOSSA	N.Q.	0.2	3.0	N.Q.	32
	EtFOSA	0.0	0.1	0.0	N.Q.	33
	MeFOSA	0.1	N.Q.	N.Q.	4.9	34
	EtFOSE	0.0	0.0	6.3	18.2	35
	MeFOSE	0.0	0.1	10.4	14.3	36
	EtFOSEA	N.Q.	0.0	N.Q.	N.Q.	37
	EtFOSEMA	N.Q.	N.Q.	N.Q.	N.Q.	38
	MeFOSEA	N.Q.	N.Q.	N.Q.	N.Q.	39
	PFOS	0.0	4.5	18.2	N.Q.	30
	Sum incl. PFOS	15.1	5.0	49.8	37.4	this study
	Total incl. PFOS	8.9****	4.7	N.A.	488.5*****	40

* The data presented is part of wastewater testing conducted in 1998, since the individual chemicals of interest were not analyzed in 1997. The 1998 data has not been adjusted for production levels in 1997, since most production remained at a similar level. It is noted that an interim carbon adsorption treatment system was installed as part of wastewater treatment in 1998, which reduced the discharge of PFOS to the Tennessee River by about half, i.e. the discharge in 1997 was likely double the amount shown here. Additionally, it is not possible to distinguish the amount of chemicals generated from specific reaction steps during production of various compounds or whether their presence may be the result of hydrolysis of more complex molecules.

** The land treatment of Decatur sludge was discontinued in early 1998. Thereafter, sludge was transported to an off-site landfill after passing through a thickener and a sludge press.

*** A review of plant records for 1998 shows that 63% of the fluorochemical containing wastes were sent to incinerators, and 33% and 4% of the wastes were disposed of in hazardous and non-hazardous waste landfills, respectively.

**** This value was estimated for 1998 after emission reduction measures took place. [27]

***** This amount was likely estimated based on the fluorine content and non-specific fluorochemical categories. [27]

The emission factors for xFOSAs and xFOSEs are derived from reported emissions to air, water and soil (through land treatment). Although indirect photolysis of EtFOSE and EtFOSA in water has been shown experimentally, the measured half-lives are rather long (> 93±10 h).[41] Thus, we assumed that all precursor substances in water ultimately volatilize into air. For those that were emitted to soil, we assumed lower and upper bounds of 20% and 80%, respectively, for the fractions that remain in soil, with the remaining fractions ultimately volatilizing into air from soil. These lower and upper bounds were applied to the emission inventory scenarios and derived from previous studies that (i) 76% of EtFOSE in an activated sludge aeration basin would be lost to the atmosphere;[42] and (ii) at 25 °C and after 120 days, about 30% and 50% of the original dose of EtFOSE is lost due to volatilization or formation of products other than those monitored in microbially active and inactive sediments, respectively.[43] Due to the significantly higher estimated yield to PFOS from xFOSA/Es in soil than in air (see Table S17), the higher inventory scenario was assigned as the 80% fraction remaining in soil (with the remaining 20% volatilizing to air). The emission factors in China for this period were assumed to remain at pre-1998 levels. Given that some of the emissions in Table S5, particularly for xFOSA/Es, were not quantified by 3M (listed as 'N.Q.'), it is possible that some emissions may have occurred but could not be considered in the calculation of the emission factors. This could have led to a slight underestimation of these emission factors (Table S4).

S2.1.3. Releases of POSF-based compounds from the use and disposal of relevant products

In contrast to releases from production sites, releases of POSF-based compounds during use and disposal are much more complex. According to 3M's sales information,[28] the majority of POSF-based products were sold to downstream industrial users who either applied them or incorporated them into their products that were then sold to end users. POSF-based compounds might therefore be released into the environment during different stages of the product life cycle including during use, further processing and disposal by downstream industrial users, during the supply chain steps between downstream industrial users and end users, and during use and disposal by end users.

3M attempted to estimate waste streams from use and disposal in 1997 in the US based on its sales data.[28] However, these estimates were normalized based on the POSF moiety ($C_8F_{17}SO_2$), making it impossible to break them down on a group basis (e.g. polymers versus non-polymers, PFOS or non-PFOS). Moreover, the assumptions made in the 3M study were not elucidated in the report and were presumably based on default engineering estimates since the work was conducted by an environmental consulting company (Battelle Memorial Institute). The estimates reported by 3M can therefore not be directly interpreted for our calculations. It is further noted that it is very difficult to estimate releases of POSF-based products (including unreacted residuals) from use and disposal using a bottom-up approach, not only because of the distinct lifetimes of an enormous variety of products and their globally widespread use, but also due to the complex pathways that may lead to environmental releases (see Figure S4).
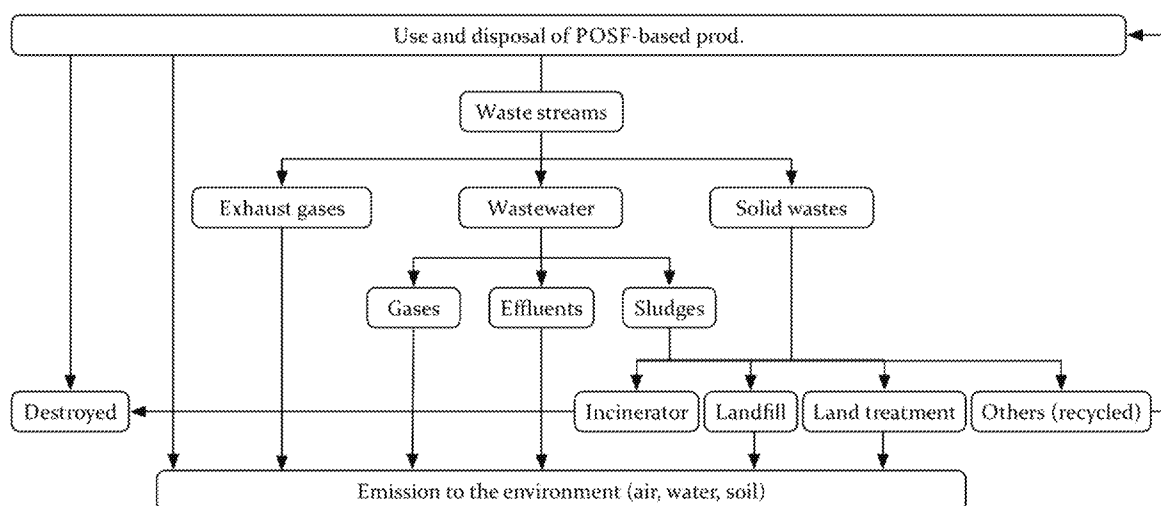
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Figure S4: Scheme of the fate of POSF-based products during use and disposal.

Depending on the use and disposal of POSF-based products, they can either be destroyed, directly emitted into the environment (air, natural water and/or soil), or discharged to the waste streams (exhaust gases, wastewater and/or solid wastes).[28] Wastewater and solid wastes containing POSF-based products are generally sent to various treatment facilities where the products may be destroyed, contained, recovered, or released into the environment. For instance, in wastewater treatment plants, a majority of POSF-based compounds are concentrated in activated sludge, whereas only a small amount remains in the aqueous phase and is released either to air during treatment processes[44,45] or to a natural water body through the effluents.[46–49] Activated sludge may be further processed for land treatment or other uses, landfilled, or incinerated. Landfilled POSF-based compounds can still be slowly released into the environment through outgassing[45] or through transport in leachates.[50] To date, no mass-balance-based study on the fate of POSF-based compounds during product use and disposal or after disposal has been undertaken. Therefore, in the next sub-sections we estimate releases of POSF-based compounds during use and disposal of POSF-based products in a generic manner with the following assumptions:

1) The proportions of polymeric and non-polymeric compounds manufactured by all manufacturers are identical and constant over a given time period.

2) Polymeric compounds do not readily degrade into non-polymeric compounds and thus do not form substantial amounts of PFSAs in a short period of time. However, polymeric products contain both PFSA impurities and unreacted residuals (e.g. xFOSA/Es) that are PFSA precursors and are steadily released over the lifetime of polymeric products.

3) Like polymeric products, non-polymeric products also contain both PFSA impurities and unreacted residuals that are PFSA precursors and are steadily released during the lifetime of non-polymeric products. In addition, some non-polymeric compounds with a complex molecular structure may break down into simpler precursor molecules (e.g. xFOSAs and xFOSEs) and then partially form PFSAs in the environment and biota after being released.

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S2.1.3.1. Non-polymeric:polymeric ratios of POSF-based compounds produced

In order to obtain temporally representative non-polymeric:polymeric ratios, we separate POSF-based compounds into two groups by taking the production history[11–13] into account (see Table S6).

Table S6: Estimated non-polymeric:polymeric ratios of POSF-based compounds produced in Japan, Western Europe, the US, and China between 1958 and 2015 in % of annual consumption. N.A. = not applicable.

	CGI (Japan, Western Europe and the US)		China	
	Non-polymeric	Polymeric	Non-polymeric	Polymeric
1958–2002	45%	55%	N.A.	N.A.
2003–2008	100%	0%	50%	50%
2009–2015	N.A.	N.A.	100%	0%

For the compounds produced prior to 2002, we estimated the ratio to be about 45% to 55% based on a series of substance flow analyses reported by 3M (see Figure S3 and Table S7).

Table S7: Estimated non-polymeric:polymeric ratios of compounds in POSF-based products in 1997 in the US (in four categories and in total) based on 3M's reports[26,27,29–40] in wt% of annual consumption.

Categories	This study								3M report *	
	Polymeric		Non-polymeric		Total		Total (normalized)		Total (normalized)	
	low	high	low	high	low	high	low	high	US	World
Aftermarket/Consumer	0.5	3.2	0.0	0.0	0.5	3.2	0.6	2.8	36.3**	48.1**
Apparel/Carpet/Textiles	43.9	58.1	0.0	0.0	43.9	58.1	52.0	50.1		
Paper and Packaging	0.2	3.2	38.6	42.4	38.7	45.6	45.8	39.3	41.2	33.3
Performance	0.9	3.2	0.4	5.9	1.4	9.1	1.6	7.8	22.5	18.6
Total	45.5	67.7	39.0	48.3	84.5	116.0	100.0	100.0	100.0	100.0
Total (normalized)	54	58	46	42	100.0	100.0	100.0	100.0	100.0	100.0

* Based on the data reported by 3M where estimates for each category were derived from the total solid weight of fluorochemical-containing compounds and have not been broken down to the POSF molecule. In contrast, our estimates in this study for each category are derived from the relative weight of the POSF molecule.

** The category "Aftermarket/Consumer" was included in the "Apparel/Carpet/Textiles" category.[29]

After 2002, producers in Japan, Western Europe and the US stepwise phased out production (ceased after 2008) and strongly reduced the use of POSF-based products: consumer applications (such as use in fabric and paper treatment, household cleaning products, pesticides and insecticides, etc.) ceased and only a few exempted industrial applications continued (such as use in metal plating, firefighting foams, hydraulic fluids, photolithography and semiconductors, etc.), where mostly non-polymeric compounds including PFOS and its salts were utilized.[51] Hence, we assumed that only non-polymeric compounds were produced between 2003 and 2008 in Japan, Western Europe and the US.

In the same period (2003–2008), China began extensively using polymeric products in textile, carpet and leather surface treatments (in a similar amount to the uses of non-polymeric products). It is reported that uses in surface treatments ceased in China after 2008 due to the global regulatory requirements,[21,22] and the remaining production of non-polymeric products in China were mainly used in metal plating, AFFF synthesis and Sulfluramid (insecticide) formulation.[21] Although EtFOSE, a raw material for the production of polymeric products, was likely still being produced in 2012 in China,[52] we assumed that POSF-based products (C$_8$) for surface treatments are produced at only a negligible level in China after 2008, since the same producers started a transition to produce PBSF- and PHxSF-based products for surface treatments in

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the same period.[52] Consequently, we changed the non-polymeric:polymeric ratios of products manufactured in China after 2008 to 100% vs 0% (see Table S6).

S2.1.3.2. Average lifetime of POSF-based products (non-polymeric and polymeric)

To our knowledge, no information on the average lifetime of POSF-based products is available, because they have been applied in countless products with very distinct lifetimes and the fractions of POSF-based products in each application field is unknown. For our calculations, we assumed an average lifetime of 10 years for polymeric products since they are designed to be durable.[53] In contrast, non-polymeric products (such as insecticides, industrial and household surfactants, and AFFF) are designed for a one-time use or multiple uses over a short period. Some non-polymeric products may have much longer lifetimes than others. For instance, some compounds were blended into paints[40] and may be released only slowly during a long lifetime of paints, and AFFFs may be stored for 5–15 years before they are used or disposed of.[53,54] To simplify the calculations, we assumed an average lifetime of 2 years for all non-polymeric products.

S2.1.3.3. Proportions of PFOS as ingredients or residuals in POSF-based products

In our calculations, we do not take into account the release of PFOS residuals from POSF-based products since the average residual level is likely very low (0.005–0.1% on a mass basis estimated by Armitage et al.[13]) and probably much lower than our uncertainty range.

In contrast, products containing PFOS and its salts as active ingredients have been produced in significant amounts for various applications (e.g., AFFF, mist suppressant in acids baths used in metal plating, photoresists and anti-reflective coatings in semiconductor usage, photomasks in semiconductor and liquid crystal industries, etching on circuit boards, photolithography, hydraulic fluids (most likely cyclic PFOS), certain medical devices, mining and oil well surfactants, alkaline cleaners, emulsifier in floor polishes, electronic components, denture cleaners, shampoos, chemical intermediates, coating additives, carpet spot cleaner, insect control, etc.).[30,31] Based on reported information, we estimated the fractions of POSF that are used to intentionally produce PFOS and its salts relative to the total POSF produced in different time periods and countries (see Table S8).

Table S8: Estimated proportions of POSF that are used to produce PFOS and its salts as active ingredients to the total POSF manufactured. CG I = Japan, Western Europe and US; N.A. = not applicable.

Period	% of total production of POSF-based species	
	CG I	China
1958–2002	5%*	N.A.
2003–2008	100%	12.5%
2009–2015	N.A.	30%

* For the years 2001 and 2002, we have adjusted the production volume of PFOS in CGI in 2001 and 2002 to 100 t/yr, which is derived from the reported minimum (50 tonnes) and maximum (160 tonnes) production volumes of PFOS in 2003.[19]

1958–2002: It is reported that less than 91 tonnes of PFOS and its salts were manufactured in 1997 in the US, of which 95% were distributed off-site for use in products and the other 5% were used on-site as an intermediate consumed to make products.[30,51] It has also been reported that about 1900 tonnes of POSF were manufactured in 1997 in the US, of which 90% were processed and sold in the US, while the remaining 10% were exported.[27,29] Hence, by assuming that all manufacturers have similar production patterns at all sites, we estimated 5% of POSF were used to produce PFOS and its salts in CGI. In the same

period, only negligible amounts of POSF-based products were manufactured in China and were therefore not taken into account. It is noted that the production of PFOS in 2001 and 2002 in CGI was likely much more than 5% of total production of POSF-based species in the same year.[19] Hence, we adjusted the production volume of PFOS in CGI during 2001 and 2002 to 100 t/yr, which is derived from the reported minimum (50 tonnes) and maximum (160 tonnes) production volumes of PFOS in 2003.[19]

2003–2008: After 3M ceased its global production of POSF-based products, the other manufacturers in CGI moved their core productions from consumer applications to industrial applications where PFOS and its salts were predominantly utilized with only limited production levels of textiles and impregnation agents existing in a few countries (see details in the review[51]). Hence, we assumed that 100% of POSF manufactured in CGI were used for PFOS and its salts. During this period, it was reported that textile treatment, metal plating, semiconductor production, and AFFFs were the main industries in China utilizing POSF-based compounds and having POSF consumption amounts of 100 t/yr, 25t/yr, 0.5 t/yr and 80 t/yr, respectively.[22] In addition, China and Brazil (using POSF imported from China) produced 3 t/yr and about 30 t/yr EtFOSA-based insecticide (Sulfluramid), respectively.[9,55] Thus, we estimated that 12.5% of POSF produced in China were used to produce PFOS and its salts based primarily on the demand from metal plating.

2009–2015: During this period, production of POSF-based products ceased in CGI, and the use of polymeric POSF-based products likely ceased in China with ongoing uses there focusing on metal plating, AFFF synthesis, and Sulfluramid formulations.[21] Consequently, we adjusted our estimate to being 30% of POSF manufactured in China was used to produce PFOS and its salts by assuming that the use of PFOS in metal plating remained at the same level as in 2009 (30–40 tonnes).[5]

S2.1.3.4. Proportions of PFCAs as impurities in POSF-based products

During the electrochemical fluorination of octanesulfonyl fluoride, some perfluorocarbon chains are unintentionally reacted to perfluoroalkane carbonyl fluorides through the electrochemical oxidation and are subsequently hydrolyzed to perfluoroalkyl carboxylic acids (PFCAs) by moist air or in the subsequent reactions.[56] Gramstad and Haszeldine isolated a 1% yield of perfluorooctanoyl fluoride from electrochemical fluorination of octanesulfonyl fluoride.[57] PFCA impurities are therefore present in all POSF-based products. Since PFCAs cannot degrade into PFSAs under any natural conditions, the fractions of PFCAs as impurities in products were subtracted from the total release of non-polymeric compounds in our calculations.

It is noted that the impurity levels of PFCAs in products vary considerably (see Table S9). Three studies determined C_5–C_{12} homologues as major PFCA impurities in commercial PFOS products,[58] ranging from 0.71 to 4.84 wt%. In another report, 3M published that their studies of eight samples have identified the presence of PFOA impurities ranging from 0.02 to 0.16 wt% in their commercial POSF-based products.[59] In addition, perfluoroalkyl carbonyl fluorides formed during the manufacture of POSF may react with reactants added during subsequent reactions of POSF and form derivatives such as perfluorooctanamides (FOAMs, $C_7F_{15}CONH(R)$, R = CH_3 or C_2H_5).[60] Jackson et al. detected varied levels of MeFOAM or EtFOAM (between 0.003 and 0.673 wt%) in eight out of ten commercial products tested.[60] The authors also found that FOAM levels are considerably lower in more recent ECF material produced in China (0.003 wt%) and in 3M's post-2001 formulations (not detected), suggesting that cleaner synthetic techniques and additional purification steps are now being used.[60] Due to lack of an analytical standard, the lower and higher homologues of FOAMs in products could be detected but not quantified.[60]

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Hence, the exact levels of PFCAs and PFCA derivatives formed during the manufacture of POSF-based products and present as impurities in these products are still unclear. In our calculations, we assumed that 1.5 wt% of PFCA-related impurities formed for the whole period (1958–2030). This is derived from the geometric mean of PFCA impurity levels listed in Table S9. The fate of these impurities is either release into the environment (for products produced prior to 2001) or removal from the products through purification procedures (for products produced after 2001). However, the fate of PFCA impurities is not within the scope of this study and is only subtracted from the estimates of POSF-based compounds and not considered further.

Table S9: Reported homologue compositions of PFCA impurities in commercial POSF-based products, in wt% of POSF-based products. N.R. = not reported; N.D. = not detected; N.M. = not measured.

Product	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	Ref.
3M PFOS	N.R.	N.R.	N.R.	N.R.	0.79	0.002	0.0005	0.0002	0.0004	N.R.	N.R.	61
PFOS (FC-95)	0.1	0.28	N.R.	N.R.	0.33	N.R.	N.R.	N.R.	N.R.	N.R.	N.R.	62
3M PFOS*	1.21	0.82	1.28	0.59	0.59	0.11	N.D.	0.24	N.M.	N.M.	N.M.	63

* Production lot #217

S2.1.3.5. Releases of PFOS and precursors during use and disposal of non-polymeric products

The estimated releases of POSF-based compounds during use and disposal of non-polymeric POSF-based products was divided into two groups: PFOS and PFOS precursors. To simplify, we did not distinguish between those as active ingredients and as unreacted residuals, but we rather assumed a lower (10%) and higher bound (100%) scenario fractions that are ultimately released into the environment during use and disposal over a product lifetime of 2 years. These lower and higher bounds may not be realistic, but they are expected to cover the range of actual emissions. In addition, we assumed a medium bound scenario that 50% of the compounds in products enter the environment, and the remaining 50% are deposited in landfills or destroyed by incineration. This was derived from a 3M report which found that about 48% of 3M's total POSF-based products sold in the US entered into wastewater and solid wastes during supply chain processing, end use, and disposal.[40] This could be considered unrealistic if AFFFs released to combat fires are not effectively recovered, landfills where wastes are disposed of are not properly designed, industrial wastewater effluents are not effectively treated, or activated sludge from wastewater treatment plants are used for land treatment, etc.

For PFOS, we assumed that all emissions enter into natural water bodies. Among PFOS precursors, many compounds with complex molecules such as EtFOSE-based phosphate diesters [SAmPAPs; such as $(C_8F_{17}SO_2N(C_2H_5)CH_2CH_2O)_2PO_2^-$] can break down into simpler molecules such as EtFOSE through biodegradation[43,64] and then form PFSAs through biotic and abiotic degradation of EtFOSE.[41,65] This can likely happen both in the real environment (soil and sediment) or in the anthropogenic environment (wastewater treatment plants and landfills). It is currently not possible to quantify the proportion of each compound (with simple structures such as xFOSA/Es or with complex structures such as SAmPAPs) emitted to each medium (air, water and soil).

As a simplification, we made the following generic assumptions:

1) For products manufactured in CGI, we assumed that 5–10% of PFOS precursors released are compounds with simple molecules (assumed as xFOSA/Es) and the rest of the 90–95% released are compounds with complex molecules, based on Figure S4. For products produced after 2008 in China (subtracting POSF exported to Brazil to make EtFOSA), we adjusted the proportions to being 45% simple molecules vs 55% complex molecules based on available use information.[21]

2) The degradation of non-polymeric compounds with complex molecules to those with simpler molecules was considered in the inventory. By looking at the molecular structures of the products by 3M (see Figure S3), most of these compounds are xFOSE-based esters. Therefore, theoretically the yields of xFOSEs from the hydrolysis of the ester bond can reach 100%. However, the fate of these non-polymers (e.g., released, incinerated, landfilled), their distribution in environmental media (e.g., soil, water, sediment) and their corresponding degradation half-lives in these media remain currently unclear. The only directly relevant study estimated that the half-life of SAmPAP (C_8) in microbially active marine sediment is likely longer than 380 days at 25°C and 3400 days at 4 °C.[43] In another study on the biodegradation of a diPAP, a fluorotelomer-based counterpart of SAmPAP, in activated sludge,[66] about 5% of the degradation product, FTOH, was observed to have volatilized in the air over the course of 92 days. In the same study, the authors suggested that the actual yields in the environment can be even higher than in the laboratory.[66] We therefore assumed that all compounds with complex molecules break down into xFOSA/Es with 2.5% and 10% volatilized in the air as the lower and higher scenarios, respectively, in the same year as they are released. The fate of the remaining 90–97.5% of xFOSA/Es generated from the degradation remains unclear in terms of their distribution among other compartments (water, soil, groundwater, sediments, etc.) and the timescale of their degradation. Therefore, they have not been included in the emission inventory calculations here.

3) The annual amounts of EtFOSA-based insecticide Sulfluramid that have been imported to, sold in, and exported by Brazil to nineteen nearby countries were considered in the inventory based on a recent study (see Table S10).[67] The insecticide is widely used to prevent leaf-cutting ants from destroying crops. We assumed linear growth from EtFOSA production of 0 t/yr in 1992 until the first recorded value of 30 t/yr identified by the study in 2004. The Brazilian production level was assumed to remain at 2013 levels in 2014 and 2015, and for the years after 2015, we assumed that EtFOSA production and application ceases (as a lower scenario) or remains constant at the 2015 level (39.7 t/yr) until 2030 (as a higher scenario). Emissions from the production of EtFOSA during the processing of POSF by Brazilian producers were assumed to be negligible, based on a report describing the process as internal and closed.[55] All Sulfluramid was assumed in the calculations to be a pure technical product and applied in the year it was sold or exported, and it was assumed that emissions during use and disposal comprised 90% of emissions to soil and the remaining 10% to air following identified interception values from pesticide application to grasslands through spraying.[68] Given that EtFOSA application in Brazil is currently dependent on POSF production in China, the higher scenario assumes that Brazil is able to produce their own EtFOSA in the years following China's predicted phase-out of POSF production.

4) With the exception of EtFOSA application, all xFOSA/Es were assumed to enter the atmosphere. Following the distribution of POSF-based products in Figure S3, 98% of all xFOSA/Es (except EtFOSA) emissions were assumed to be xFOSEs and the remaining 2% were assumed to be xFOSAs. Emissions of PFOS, both direct and residuals, were assumed to enter surface water.

Table S10: Estimated total amounts (in tonnes) of EtFOSA in Brazil from import and production between 1993 and 2015 based on a recent study[67] and using our assumption of a linear growth from 0 t/yr in 1992 to the 30 t/yr in 2004 identified by the study.[67]

Year	EtFOSA [t]	Year	EtFOSA [t]	Year	EtFOSA [t]
1993	2.5	2001	22.5	2009	23.3
1994	5	2002	25	2010	30.9
1995	7.5	2003	27.5	2011	36.0
1996	10	2004	30	2012	31.8
1997	12.5	2005	30	2013	40.6
1998	15	2006	31	2014	40.1
1999	17.5	2007	31	2015	39.7
2000	20	2008	30		

S2.1.3.6. Release of residuals from use and disposal of polymeric POSF-based products

For polymeric products, we focused on quantifying the release of residuals only, as the fate and transport of polymers, including degradation, still have great uncertainties. Several studies have been conducted to measure the levels of selected non-polymeric residuals in various polymeric and non-polymeric POSF-based products, and they suggest that the levels vary considerably (see Table S11). We assumed that non-polymeric residual levels range from 0.1 to 5% (by mass) as the lower and higher scenarios, respectively. During use and disposal of polymeric products, (semi)volatile residuals are steadily emitted into air, and non-volatile residuals are released into the wastewater or solid wastes being treated, landfilled, or incinerated. Due to a lack of information, we can assess neither the proportions of (semi)volatile and non-volatile residuals remaining in the products nor the absolute proportions of residuals that are emitted into the environment. However, a study[69] detected semi-volatile MeFOSE and EtFOSE being the predominant residuals in 3M apparel/carpet/textile products and having a much higher concentration (by a factor of about 100) than the other detected residuals. Hence, we applied the assumption that 98% of non-polymeric residuals in polymeric products are semi-volatile xFOSEs and 2% are semi-volatile xFOSAs that are 100% steadily volatilized into air over the generic product lifetime of 10 years, although this might be an overestimation of actual emissions.

Table S11: Reported residual levels (on a mass basis) in POSF-based products. N.A. = Not available.

Categories	Site	Sample Nr.	Lower	Higher	Aver.	Ref.
Paper and Packing	UK	N.A.	N.A.	1.0%	N.A.	15
Total POSF-based Prod.	UK	N.A.	0.0%	7.0%	2.4%	15
Total POSF-based Prod.	Global	N.A.	0.1%	3.0%	N.A.	11
3M Carpet Treatment Prod.	Global	N.A.	0.3%	5.0%	N.A.	26
Total 3M Prod.	Global	N.A.	N.A.	N.A.	1-2%	26
3M Apparel/Carpet/Textiles Prod.	Global	8	0.7%	5.3%	N.A.	69

S2.1.3.7. Indirect emissions of PFOS from degradation of non-polymeric species

We considered the formation of PFOS in the environment and biota from degradable POSF-based compounds, namely from non-polymeric compounds released from production sites (estimated in section S2.1.2) and from non-polymeric compounds as ingredients or residuals released during use and disposal of both polymeric and non-polymeric products (estimated in sections S2.1.3.5 and S2.1.3.6). Degradation of non-polymeric compounds may involve different mechanisms with distinct degradation products and yields dependent on the physicochemical properties of each compound and on the media. For instance, semi-volatile POSF has a low water solubility (<294 ng/ml)[70] and likely stays in air where it does not react with OH radicals[71] but can be hydrolyzed by moist air and form PFOS.[57] Semi-volatile xFOSEs have rather high air-water partition coefficients[72] allowing a fraction of them in wastewater and solid waste to volatilize into air[44,45] and partially degrade into PFOS by OH-radical oxidation.[65] xFOSEs that accumulate in sludge undergo aerobic microbial biodegradation to form PFOS.[42,73,74] In vitro and in vivo tests also show that biodegradation of EtFOSE takes place in biota and forms PFOS.[75,76] Furthermore, non-polymeric compounds with complex molecules such as SAmPAPs may break down into simpler molecules such as EtFOSE through biodegradation[43,64] and then form PFOS through biotic and abiotic degradation.[41,65]

The cumulative degradation of xFOSA/Es and POSF to PFOS was estimated using the CliMoChem global multimedia mass-balance model. In the model's calculations, it considers values for each of the degradation half-lives and yields for POSF, xFOSAs, and xFOSEs in individual environmental compartments. These model inputs are shown and discussed in section S3.3.

S2.1.4. The homologue compositions of POSF-based products

For POSF and PFOS emitted to the environment, we assumed that they have the same homologue composition as commercial PFOS products (see Table S12). In our calculations, we assumed that the geometric and arithmetic means represent the lower and higher scenarios, respectively.

Table S12: Reported homologue compositions in two commercial PFOS-based products, in % (on a mass basis) of PFOS-based products. N.R. = not reported; N.D. = not detected; N.M. = not measured.

Product	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	Ref.
NH4-PFOS, FC-93 *	0.1–2	0.1–2	0.1–2	0.1–2	19–23	N.R.	N.R.	77
PFOS, Lot #217	1.72	N.M.	7.31	N.M.	86	N.M.	N.D.	63
arithmetic mean	3.3	4.1	5.2	4.1	84.7	1 **	1 **	this study
geometric mean	1.1	0.99	1.8	0.9	84.5	0.1 **	0.1 **	this study

* This product is diluted in solvents; the intended content of PFSAs is 25%. We therefore multiply each range by 4.
** The actual levels have not been reported and therefore the arithmetic and geometric mean cannot be calculated. In our calculations, we assumed the lower and upper bounds (0.1% and 1%) as the lower and higher scenarios.

Similarly, for xFOSA/Es released into the environment, we assumed they have the same homologue composition as the commercial products that contain xFOSA/Es as main ingredients (see Table S13). In our calculations, we used the minimum and maximum values as the lower and higher scenarios.

Table S13: Reported homologue compositions in various commercial POSF-based products, in % (on a mass basis) of xFOSA/E-based products. N.R. = not reported; N.D. = not detected; N.M. = not measured.

Product	C$_4$	C$_5$	C$_6$	C$_7$	C$_8$	C$_9$	C$_{10}$	Ref.
EtFOSE, L-10059, FM-3422	0.11	0.03	0.51	0.82	96.09	N.R.	N.R.	78,79
EtFOSE, Lot 547, FM-3924	1.52	1.34	3.52	1.40	87.16	N.R.	N.R.	78,79
EtFOSE, FC-10	2–6	1–3	3–7	2–6	80–90	N.R.	N.R.	80
MeFOSE, L-1276	1.62	1.34	5.05	1.69	83.88	0.87	N.R.	78
EtFOSA, FX-12	N.R.	N.R.	N.R.	1.1–6	93–98.9	N.R.	N.R.	81
EtFOSEA, FX-13, 423-82-5	4–6	1–3	3–5	2–4	83–85	N.R.	N.R.	82
EtFOSEMA, FX-14, 376-14-7	4–6	1–3	3–5	2–4	83–85	N.R.	N.R.	83
FC-171, CAS 68958-61-2	N.R.	N.R.	N.R.	1.1–6	89–97.9	N.R.	N.R.	84
FC-750, CAS 1652-63-7 *	1–4	0.1–1	1–5	1–4	40–44	N.R.	N.R.	85
FC-170C, CAS 29117-08-6 *	3–7	0.5–1.5	3–7	1–5	68	N.R.	N.R.	86
FC-135, CAS 1652-63-7 *	1–4	0.1–2	1–5	1–4	40–44	N.R.	N.R.	87
FC-129, CAS 2991-51-7 *	1–5	N.R.	1–5	1–3	40–60	N.R.	N.R.	88
lower scenario	0.11	0.03	0.51	0.82	80	0.87	0.1 **	this study
higher scenario	6	3	7	6	98.9	1 **	1 **	this study

* These products are diluted in solvents and were not taken into account for the lower and higher scenarios.
** The levels of C$_9$ and C$_{10}$ homologues have not been reported. In our calculations, we assumed a lower and upper bound (0.1% and 1%) as the lower and higher scenarios.

S3. Parameterizations for the CliMoChem model

S3.1. Overview of the model

The CliMoChem model was used for the global fate modeling of the emission inventory in this study, and the main details of the model are explained in the section *Modeling environmental concentrations and fluxes over time* in the main text.

S3.2. Mode of entry and geographical distribution of emissions

The distribution of emissions from CGI countries followed those applied by Armitage et al.[13] 50% of emissions in CGI from manufacturing were assumed to enter Zone 3 (36–54°N) and the other 50% to Zone 4 (18–36°N). This is based on the location of the two main manufacturing facilities in Antwerp, Belgium and Decatur, Alabama. Use and disposal emissions from products made in CGI were distributed 90% to Zone 3 and 10% to Zone 4 where most of the products were assumed to have been marketed (e.g., Western Europe, North America, Japan).

For the remaining source countries, we made use of new distributions. The distribution of emissions from POSF-based product manufacturing in China was based on estimated emissions by Chinese region[21] (30% to Zone 3 and 70% to Zone 4). The same proportion was used for the distribution of emissions from the use and disposal of these Chinese products. Furthermore, emissions from the production of EtFOSA (Sulfluramid) in Brazil were assumed to be negligible,[55] and zone assignments were therefore not applicable. For the emissions of EtFOSA from the use and disposal of Sulfluramid in Brazil, just over 52% and 47% were assigned to Zone 6 (0-18°S) and Zone 7(18-36°S), respectively, whereas less than 1% were assigned between Zones 3, 4, and 5, based on small quantities exported from Brazil to other countries. This distribution is based on a recent study[67] detailing Sulfluramid sold in Brazilian states and exported abroad.

S3.3. Substance properties and degradation fractions of formation

Degradation rates, partition coefficients, and fractions of formation were defined in the model for POSF, PFOS, xFOSAs, xFOSEs, and intermediates (INT). These were defined at higher and lower levels to cover the range of potential values and support the creation of the higher (fast) and lower (slow) scenarios. Table S14 and show the half-lives used to define the slow and fast degradation rate constants in the model runs, respectively, as well as their corresponding literature references, with details elaborated below. We applied many of the same partition coefficients and degradation rate constants for the substances as used in the model runs of Schenker et al.[89] and Armitage et al.[13]. However, we made some adjustments to reflect newer empirical findings and have additionally considered degradation in the soil and water compartments.

1) The hydrolysis half-life of POSF to PFOS is unknown. An early study shows that only 10% of POSF underwent hydrolysis after being heated with water at 180 °C for three days.[57] Hence, it is likely that the half-life in the environment is much longer than three days. We assumed a half-life of 0.5 (fast degradation) and 5 years (slow degradation) for POSF across all compartments, respectively.

2) PFOS was assumed to not degrade under natural conditions[90] (half-life was set towards infinity at a value of 10^{19} days).

3) A long half-life of one year in soil was set for xFOSAs, following the assumption in Gilljam et al.,[67] and a short half-life of 13.9 days was set based on measurements in aerobic soil by Avendaño et al.[91] To our best knowledge, studies on the degradation of xFOSAs in water were not identified; however, this process was assumed negligible given the substance's tendencies to partition to air and organic matter. The assumed short and long half-lives of xFOSAs in air were derived from the average value of 28.6 days from Martin et al.[92]

4) The short and fast half-lives used for xFOSEs in soil are based on the upper and lower bound experimental results obtained in marine sediments by Benskin et al.[43] The half-lives of xFOSEs in water were taken from two studies completed by 3M.[93,94] The half-life of xFOSEs in air were taken from the results of D'eon et al.[65]

5) Given the inconclusive results of recent studies regarding the ability of perfluoroalkyl compounds to be metabolized by vegetation,[95,96] we took the possibility into account by assuming vegetative degradation is equal to the degradation rate in water for the fast degradation scenario (Table S15)

6) The half-lives for the intermediate compound (INT) were taken from Schenker et al.[89]

7) Second order rate constants for atmospheric degradation are calculated from these half-lives assuming an OH radical concentration of 7.5×10^5 molecules/cm^3.

Table S14: Half-lives ($t_{1/2}$) in days used to define the slow degradation rate constant set in the model for each substance and compartment. Corresponding references are shown as superscripts, and values that have been updated or newly considered in comparison to those used in Armitage et al. are in *italics*. 1.00E+19 = 10^{19}.

Substance	$t_{1/2}$ soil [d]	$t_{1/2}$ water [d]	$t_{1/2}$ air [d]	$t_{1/2}$ vegetation [d]
POSF	*1825*	*1825*	*1825*	1.00E+19
PFOS	1.00E+19	1.00E+19	1.00E+19	1.00E+19
xFOSAs	*365*[67]	1.00E+19	*40*[92]	1.00E+19
xFOSEs	*160*[43]	*2665*[93,94]	*1.8*[65]	1.00E+19
INT	1.00E+19[89]	1.00E+19[89]	28.6[89]	1.00E+19

Substance	$t_{1/2}$ soil [d]	$t_{1/2}$ water [d]	$t_{1/2}$ air [d]	$t_{1/2}$ vegetation [d]
POSF	*180*	*180*	*180*	*180*
PFOS	1.00E+19	1.00E+19	1.00E+19	1.00E+19
xFOSAs	*13.9*[91]	1.00E+19	*20*[92]	1.00E+19
xFOSEs	*44*[43]	*2300*[93,94]	*1.8*[65]	*2300*
INT	1.00E+19[89]	1.00E+19[89]	28.6[89]	1.00E+19

Table S16 shows the partition coefficients and activation energies used as inputs for each substance:

1) The partition coefficients for POSF was calculated using COSMOtherm following the method in Wang et al.[72] Following Armitage et al.,[13] PFOS was set to have an octanol-water partition coefficient (log K_{OW}) of 2.9 and a very low air-water partition coefficient (log K_{AW}) following the assumption that PFOS is in its non-volatile anionic form. Partition coefficients for xFOSEs and xFOSAs were set as the averaged values of MeFOSE and EtFOSE and of MeFOSA and EtFOSA, respectively, estimated by Wang et al.[72]. Properties for the intermediate substance (INT) were taken from Schenker et al[89] and as used in the calculations by Armitage et al.[13]

2) The energy of activation (*EA*) for the degradation reaction is defined by compartment (soil, water, air, and vegetation (veg)). The energy of activation for the degradation reaction in soil, water, and vegetation was set to 30000 J/mol following Armitage et al.[13] The energy of activation for degradation in air for POSF and PFOS follow Armitage et al.,[13] whereas the value of 5000 for xFOSAs is taken from Wang et al.[97] and is assumed to also represent xFOSEs. This particular value for xFOSAs and xFOSEs may be an overestimation; however no additional published values were found suggesting a more accurate activation energy.

3) The internal energy of phase change between octanol and water (ΔU_{OW}) of -20000 J/mol as well as the values for internal energy of phase change between air and water (ΔU_{AW}) were calculated for the substances based on the method from MacLeod et al.[98]

Table S16: Model partition coefficients and activation energies for each substance.

Substance	logK_{AW}	logK_{OW}	EA_{SOIL} [J]	EA_{WATER} [J]	EA_{AIR} [J]	EA_{VEG} [J]	ΔU_{AW} [J/mol]	ΔU_{OW} [J/mol]
POSF	4.41	3	30000	30000	15000	30000	11612	-20000
PFOS	-8	2.9	30000	30000	15000	30000	84442	-20000
xFOSAs	-0.47	6.39	30000	30000	5000[96]	30000	48863	-20000
xFOSEs	-2.22	6.26	30000	30000	5000	30000	63069	-20000
INT	-0.5	5.94	30000	30000	2500	30000	45213	-20000

We defined the fractions of formation (i.e., yields) from degradation of the substances in the model separately for each environmental compartment (see Table S17):

1) For the air compartment, we follow the simplified atmospheric degradation scheme proposed by Schenker et al.[89] as shown in Figure S5. The approach only explicitly considers compounds that are stable for several hours, and it groups similar substances into "blocks", which are defined by an average set of physicochemical properties. In this study, we used the xFOSE, xFOSA, and intermediate (INT) blocks. The simplified degradation scheme is shown in part B of Figure S5. The path to PFOS begins with degradation of xFOSE, which leads either to a radical that can

further transition to PFOS or to xFOSA that can then degrade to PFOS via a radical or the INT. The fractions along each step of the pathways are defined in the figure. The overall yield from xFOSE to PFOS ranges and is based on two smog chamber studies on the OH radical oxidation of EtFBSA and MeFBSE, respectively.[65,92] D'Eon et al. reported that after 50% consumption of MeFBSE, a large amount of MeFBSA formed and the concentrations of C_2–C_4 PFCAs and PFBS accounted for approximately 10% and 1% of the loss of MeFBSE, respectively.[65] Martin et al. reported 45% of the EtFBSA transferred into C_2–C_4 PFCAs.[92] Based on this, we used a lower and upper bound of 1% and 4.5% for the overall yields of PFOS from the degradation of xFOSEs, respectively. Using this scheme, the upper and lower yields of degradation from each parent compound to its daughter compound were mathematically solved for this overall range (see Table S17).

2) For the soil compartments (soil and vegetative soil), the yield range for xFOSE to xFOSA and PFOS is based on empirical observations in active marine sediments at 4°C and 25°C after 120 days by Benskin et al.[43]. The higher yield for xFOSA to PFOS is based on empirical observation in aerobic soil after 182 days by Avendaño et al.[91], whereas a lower yield of 0.1% was assumed given the lack of empirical studies.

3) For the snow and ice compartments, all yields were set to zero since degradation is assumed to not occur therein. For the water compartment, we used the same yields as those for the air compartment, as degradation in both media involve OH-radical-mediated pathways with possible, unknown differences. For the vegetation compartment, the higher yield was set equal to that of water following the uncertainty regarding degradation in vegetation that was discussed previously. All degraded POSF was set to yield PFOS.
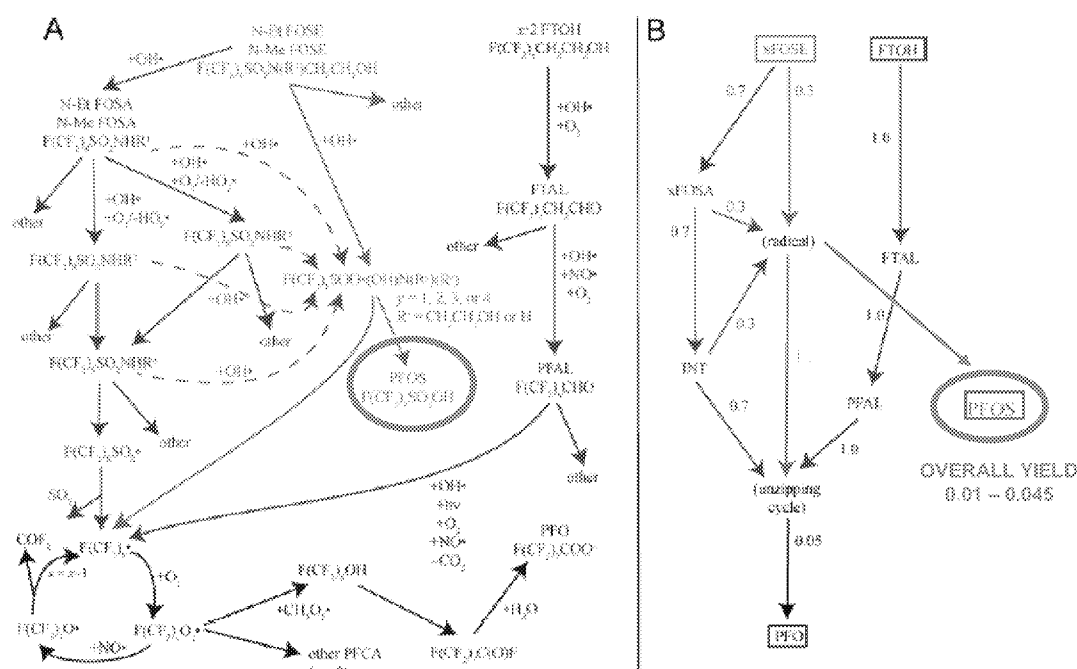
Figure S5: The degradation scheme of FTOH and POSF-based precursors in the atmosphere as adapted from Schenker et al.[89] and used previously in Armitage et al.[13] (A) a summary of the key reactions with intermediate degradation products, (B) the simplified degradation scheme applied in the model of the present study. Substances in parentheses were not explicitly modeled. Substances in rectangles have direct emissions into the environment. Numbers next to an arrow represent fractions of formation.

Table S17: Estimated fractions of formation (i.e. yields in mol%) for degradation of each parent compound to its daughter compound.

Environmental Compartment	Parent Compound	Daughter Compound	Lower Yield	Higher Yield
Air	xFOSA	INT	0.7	0.7
Air	xFOSA	PFOS	0.00456	0.02055
Air, Water	xFOSE	xFOSA	0.7	0.7
Air, Water	xFOSE	PFOS	0.00456	0.02055
Air	INT	PFOS	0.00456	0.02055
Soil	xFOSA	PFOS	.001	.04
Soil	xFOSE	PFOS	.0044	.12
Soil	xFOSE	xFOSA	.017	.064
Vegetation	xFOSE	xFOSA	0	0.7
Vegetation	xFOSE	PFOS	0	.02055
Vegetation	POSF	PFOS	0	1
Air, Soil, Water	POSF	PFOS	1	1

S3.4. Model runs

In order to identify the potential ranges of modelled environmental concentrations, model runs with different combinations of parameters were conducted taking each substance and environmental compartment into account. Table S18 shows the detailed combinations of the higher, medium and lower emission inventory scenarios with the faster or slower degradation and lower or higher yields needed to create the high, medium, and low bounds of modeled environmental concentrations.

The medium and lower emissions inventories were developed using the lower range of all input variables, with the medium inventory assuming that 50% of the produced compounds are released into the environment during the use and disposal phase, and the lower inventory assuming that 10% are released during the use and disposal phase. The higher emission inventory was developed using the higher range of all input variables and assuming that 100% of the produced compounds are released into the environment during the use and disposal phase.

Table S18: Combinations of model parameter sets used to define the higher, medium, and lower scenarios of modeled environmental concentrations for PFOS in water, xFOSA/Es in the atmosphere, and PFOS flux to the Arctic.

Modeled Scenarios	PFOS in Water	xFOSA/Es in Air	PFOS Flux to Arctic
Higher	higher inventory, faster degradation, higher yield	higher inventory, slower degradation, lower yield	higher inventory, faster degradation, higher yield
Medium	medium inventory, slower degradation, lower yield	medium inventory, faster degradation, higher yield	medium inventory, faster degradation, higher yield
Lower	lower inventory, slower degradation, lower yield	lower inventory, faster degradation, higher yield	lower inventory, slower degradation, lower yield

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S4. Comparison to field measurements

In order to evaluate the emission inventory, modeled environmental concentrations were compared to reported field measurements of PFOS, xFOSAs, and xFOSEs in literature and other sources. The field measurements included in the comparison cover multiple regions of the world, and many were completed during sea sampling campaigns on research vessels. Some of the air samplings for xFOSAs and xFOSEs were completed at stationary research sites in the Arctic. Only measured sites that are most representative of background concentrations were considered. For example, sites on industrialized land, surrounded by industrialized land (e.g., the North, Baltic, and South China Seas), near known point sources, or suspected to have been affected by abnormal events were not considered. Abnormal events, such as floods, have been previously reported to affect measured concentrations.[99] One study[100] found extraordinarily high concentrations of PFOS in oceanic surface water during a sampling cruise in the Southern Atlantic Ocean. Given that these measurements were anomalously magnitudes larger than concentrations reported by other studies in the same area, these sampling points were not considered for our model evaluation.

Atmospheric concentrations of xFOSA are represented by the sum of measured MeFOSA and EtFOSA concentrations. Atmospheric concentrations of xFOSE are represented by the sum of measured MeFOSE and EtFOSE concentrations. Some studies considered both gaseous and particulate concentrations of xFOSA/Es, while others considered only gaseous concentrations. This difference is shown on the plots comparing the model results to the field measurements. Only field measurements above the limit of quantification (LOQ) published in a study were included in the plots of results.

The field studies considered are listed in the references.[100-114] Measurement data from the Alert Station in Canada were provided thanks to Dr. Hayley Hung from Environment Canada and collected under Canada's Northern Contaminants Program (NCP) and Chemicals Management Plan (CMP). Air measurement data from the Villum Research Station in Greenland were also considered and provided thanks to Dr. Rossana Bossi from Aarhus University.

S5. Additional results that supplement those included in the main publication

S5.1. Calculation on a homologue basis

Table S19: Global emissions of C_4–C_{10} PFSAs, xFASA/Es, and PASFs from the life cycle of POSF-based products in the years 1958-2002, 2003-2015 and post 2015 in tonnes.

PFSAs (Based on PFOS emissions)

C_n PFSA	1958-2002 [t]		2003-2015 [t]		2016-2030 [t]		Total [t]	
	Lower	Higher	Lower	Higher	Lower	Higher	Lower	Higher
C_4 PFBS	13	132	1	26	0	5	14	163
C_5 PFPeS	10	164	1	32	0	6	11	202
C_6 PFHxS	21	208	2	40	0	8	23	256
C_7 PFHpS	10	164	1	32	0	6	11	202
C_8 PFOS	981	3393	75	656	8	123	1064	4172
C_9 PFNS	1	40	0	8	0	1	1	49
C_{10} PFDS	1	40	0	8	0	1	1	49

xFASA/Es (Based on xFOSA/Es emissions)

C_n xFASA/Es	1958-2002 [t]		2003-2015 [t]		2016-2030 [t]		Total [t]	
	Lower	Higher	Lower	Higher	Lower	Higher	Lower	Higher
C_4 FBSA/Es	1	472	1	58	0	42	2	572
C_5 FPeSA/Es	0	236	0	29	0	21	0	286
C_6 FHxSA/Es	5	551	2	68	0	49	8	668
C_7 FHpSA/Es	9	472	4	58	0	42	13	572
C_8 FOSA/Es	846	7780	384	958	4	698	1234	9436
C_9 FNSA/Es	9	79	4	10	0	7	13	95
C_{10} FDSA/Es	1	79	0	10	0	7	2	95

PASFs (Based on POSF emissions)

C_n PASF	1958-2002 [t]		2003-2015 [t]		2016-2030 [t]		Total [t]	
	Lower	Higher	Lower	Higher	Lower	Higher	Lower	Higher
C_4 PBSF	8	25	0	1	0	0	9	27
C_5 PPeSF	7	32	0	1	0	0	7	33
C_6 PHxSF	14	40	1	2	0	1	14	42
C_7 PHpSF	7	32	0	1	0	0	7	33
C_8 POSF	652	653	24	25	2	9	678	687
C_9 PNSF	1	8	0	0	0	0	1	8
C_{10} PDSF	1	8	0	0	0	0	1	8

S5.2. Inventory comparison to previous studies

In addition, we compared our developed emission inventory with those developed previously by Armitage et al.[13] and Paul et al.[12]

Table S20: Global emissions of PFOS, xFOSA/Es, POSF, and POSF derivatives from the life cycle of POSF-based products in this study compared with results from Armitage et al. [13] and Paul et al.[12] (in tonnes).

	Paul et al.[12]	Armitage et al.[13]	This Study			
	1970 - 2002	1957 - 2010	1958 - 2002	2003 - 2015	2016 - 2030	Total
PFOS						
1. Emissions from production	7 - 130	75 - 299	714 - 716	27 - 28	2 - 10	743 - 754
2. Emissions from use and disposal	446 - 2150	275 - 2785	267 - 2677	48 - 628	6 - 113	321 - 3418
3. Emissions from degradation of xFOSA/Es*	-	3 - 168	5 - 337	1 - 36	0 - 25	6 - 398
4. Emissions from degradation of POSF*	-	-	160 - 491	6 - 17	0 - 5	166 - 513
Total	452 - 2730	353 - 3252	1146 - 4221	82 - 709	8 - 153	1236 - 5083
xFOSA/Es						
1. Emissions from production	-	681 - 905	557 - 689	21 - 26	2 - 10	580 - 725
2. Emissions from use and disposal (excluding Brazil)	-	64 - 3146	175 - 6950	13 - 500	2 - 78	190 - 7528
3. Emissions from application in Brazil	-	-	114 - 141	350 - 432	0 - 610	464 - 1183
Total	-	745 - 4051	846 - 7780	384 - 958	4 - 698	1234 - 9436
POSF						
1. Emissions from production	-	-	652 - 653	24 - 25	2 - 9	678 - 687
POSF-derived products and precursors						
1. Emissions from production	650 - 2600	-	-	-	-	-
2. Emissions from use and disposal	4200 - 42000	-	-	-	-	-

*These values were estimated by the CliMoChem model.

Table S20 shows the emission values of our inventory between 1958–2002 in comparison with those between 1957-2010 in Armitage et al. and between 1970-2002 in Paul et al. We estimate substantially higher PFOS emissions from production than in both previous studies mainly resulting from updated emission factors from production sites including new consideration of land treatment using contaminated sludge. While Paul et al. did not estimate precursor degradation into PFOS, our estimated precursor degradation into PFOS is greater than Armitage et al. due to the consideration of additional degradation pathways in soil and higher estimated precursor releases during the use and disposal phase. For xFOSA/Es, our estimates of emissions from production are lower than Armitage et al. due to our revised emission

factors (i.e., separation of emission factors for PFOS and xFOSA/Es based on 3M's reports instead of using assumptions as in Armitage et al.), whereas our estimates for the use and disposal phase are substantially higher in the upper bound estimates (due to our expanded estimation of PFOS precursors as elaborated in the *Methods* section; see also Section S2.1.3.5 in the *SI*). Paul et al. estimate the release of POSF-derived products (representing all secondary reaction products and precursors) into the environment from the production and use and disposal phases. They note that "3M's official figures give estimated environmental releases of 76 t of POSF to air and 4,200 t to water, based on conservative, worst case scenarios assuming that all POSF products and residuals completely breakdown to PFOS." Paul et al. further state that, "Here, the estimated emissions are revised upward to give 235 t to air and 42,000 t of POSF to water (see Table 1)." These up-scaling factors of 4 and 10 are unclear, along with some others, making a more in-depth comparison of our results with their results challenging.

S5.3. Calculation of PFOS deposition fluxes to the Arctic

We used the CliMoChem model results to estimate the annual fluxes of PFOS to the Arctic based on our emission inventory. An Arctic surface area of 26.4 million square kilometers was used in the calculations as based on Schenker et al.[89] with the Arctic region defined as being north of 65 degrees north latitude. The total deposition fluxes from air to snow and ice (diffusion, dry deposition, wet deposition, and rain deposition) in zone 1 and in 39% of zone 2 were used in defining the fluxes. Our modeled fluxes were compared to estimated fluxes into snow from the snow pit measurements at the Devon Ice Cap by Young et al.[115] and by MacInnis et al.[116] For comparison, we expanded the estimated fluxes per square meter from these studies to the area of the Arctic used in our model calculations. Figure S6 shows the comparison of modeled annual fluxes of PFOS to the Arctic via air (with and without considering POSF emissions) with the fluxes estimated from field measurements in these two studies.
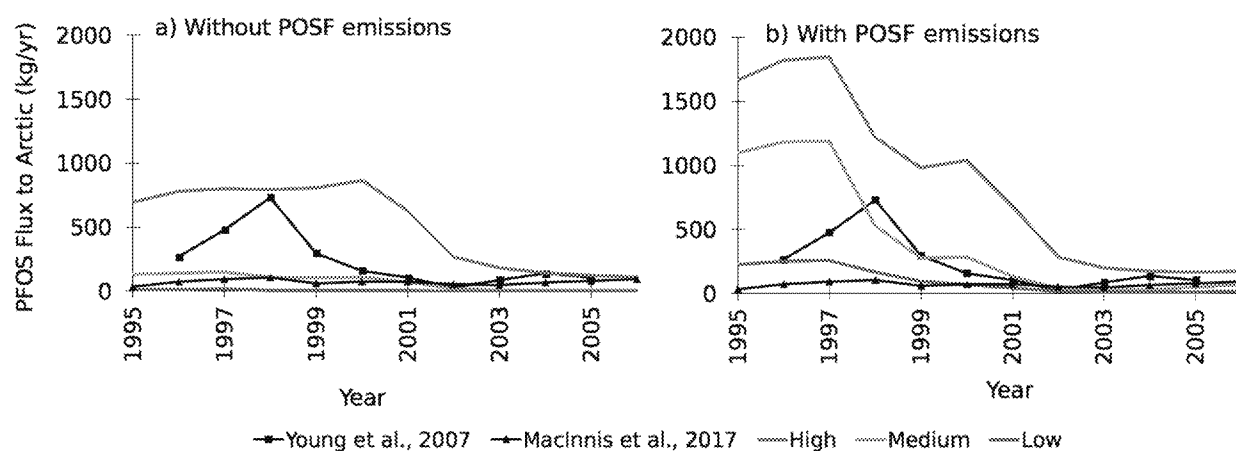

Figure S6: Modeled annual PFOS deposition fluxes to the Arctic based on our emission inventory (left: without considering POSF emissions; right: with considering POSF emissions) in comparison to estimated annual fluxes based on field measurements taken at the Devon Ice Cap.[115,116]

S5.4. Calculation of permanent losses of substances in the ice and water compartments

The model calculates significant permanent losses of substances in the ice and water compartments (i.e., loss to the deep ocean and sedimentation to the ocean floor). Table S21 shows these calculated losses for each scenario combination. This helps to explain, for example, the emitted POSF that does not degrade into PFOS as shown in Table 2 of the main publication.

Table S21: Total calculated permanent losses of POSF, PFOS, xFOSAs, and xFOSEs in the model for the years 1958 to 2030 in tonnes by scenario combination in the water and ice compartments.

Substance name and compartment of permanent loss	Higher inventory, faster degradation, higher yield	Higher inventory, slower degradation, lower yield	Medium Inventory, faster degradation, higher yield	Lower inventory, faster degradation, higher yield	Medium inventory, slower degradation, lower yield	Lower inventory, slower degradation, lower yield
POSF to Water	0.0	0.1	0.0	0.0	0.1	0.1
POSF to Ice	162.6	515.4	160.4	160.4	508.6	508.6
PFOS to Water	94.9	73.6	48.3	24.8	41.1	19.3
PFOS to Ice	7.6	2.1	4.7	4.4	1.5	1.5
xFOSAs to Water	104.0	158.5	19.7	9.8	31.6	17.1
xFOSAs to Ice	176.2	264.6	31.8	14.8	51.1	26.8
xFOSEs to Water	488.8	495.5	96.3	51.0	97.6	51.7
xFOSEs to Ice	78.8	78.9	12.4	4.7	12.4	4.7

S5.5. Additional modeled environmental concentrations

Figure S7 through Figure S9 show modeled environmental concentrations of PFOS in water and *x*FOSAs/*x*FOSEs in air in comparison to reported field concentrations[100–113] for modeled zones not included in the main publication. Table S22 shows details regarding the number of field measurements within the modeled range.
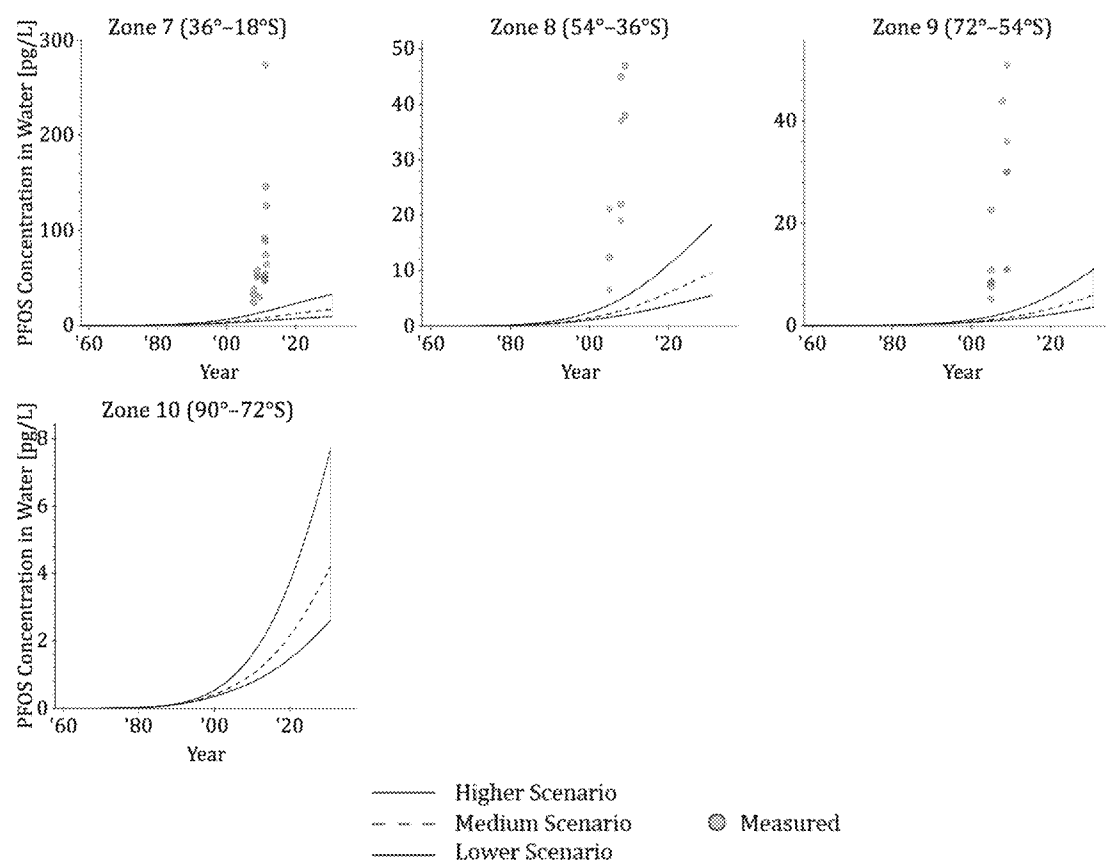

Figure S7: Modeled vs. measured field concentrations for PFOS in oceanic surface water between 1958–2030 in zones 7–10. Results from the higher, medium, and lower model scenarios are shown.
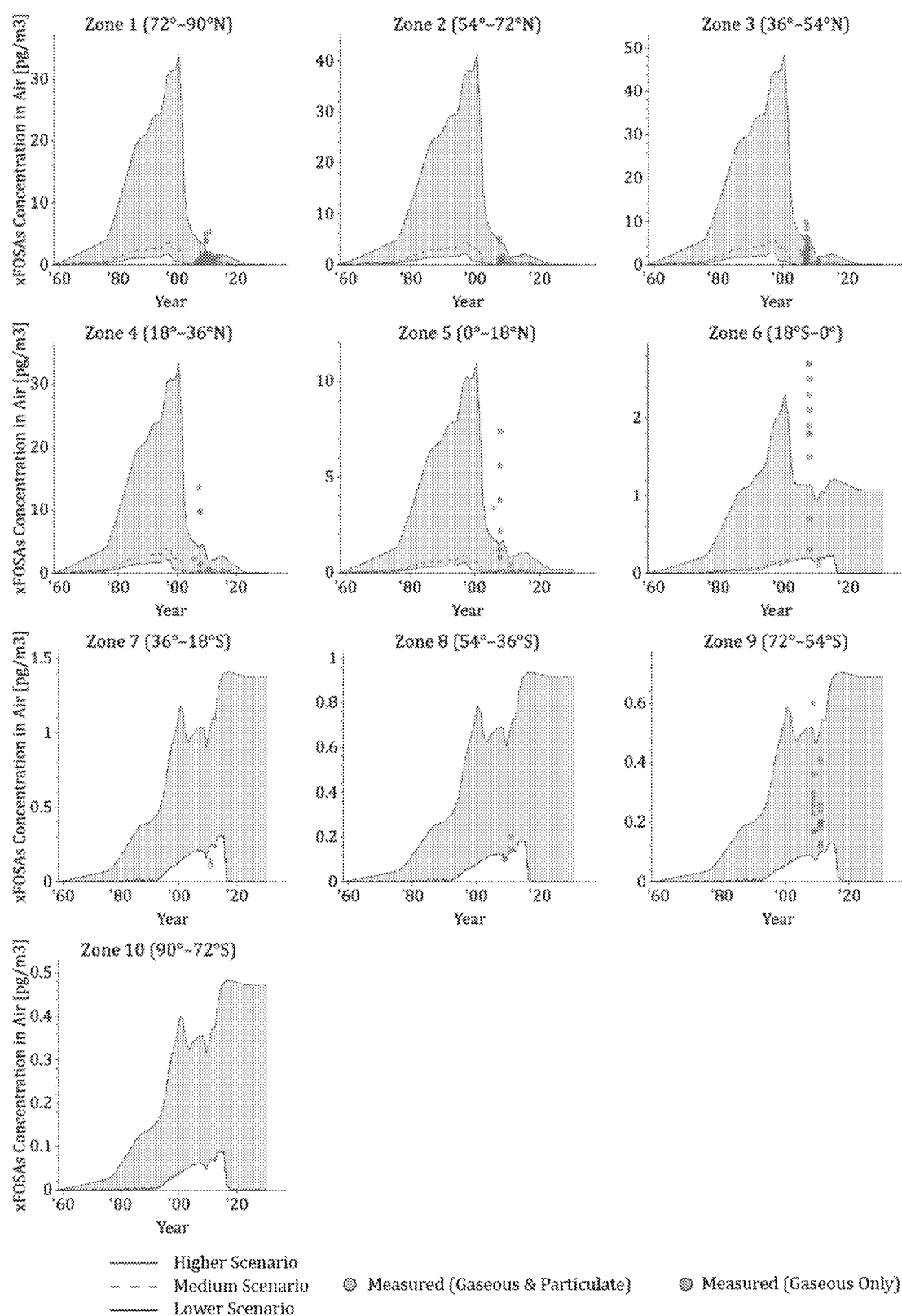
Figure S8: Modeled vs. measured field concentrations for xFOSAs in the air between 1958–2030 in zones 1–10. Annually averaged results from the higher, medium, and lower model scenarios are shown.
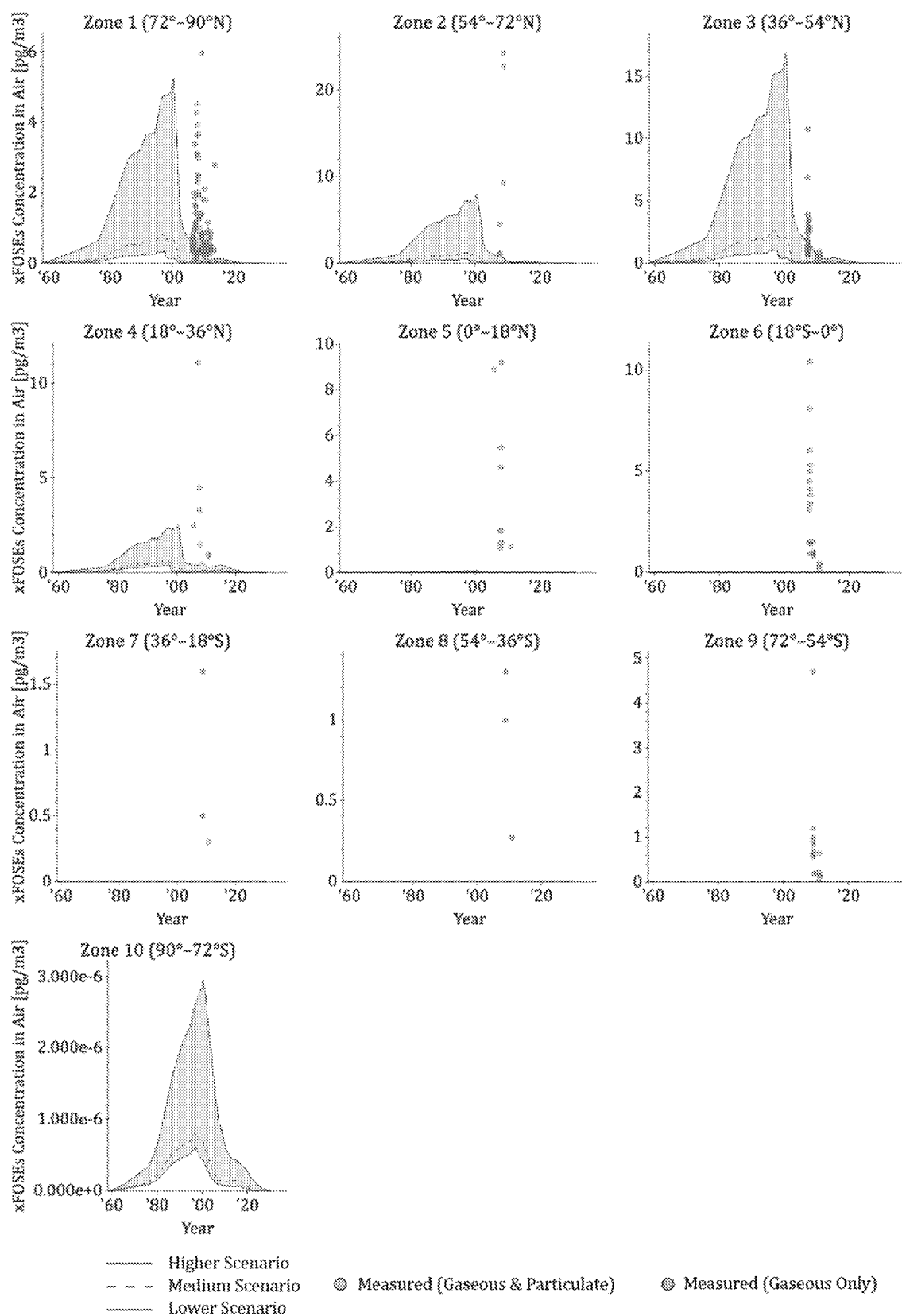
Figure S9: Modeled vs. measured field concentrations for xFOSEs in the air between 1958–2030 in zones 1–10. Annually averaged results from the higher, medium, and lower model scenarios are shown.

Table S22: The numbers of reported measurements of PFOS, *x*FOSAs, and *x*FOSEs in each zone that were compared with modeled environmental concentrations. The numbers of the measurements that were below the limit of quantification (LOQ) of the corresponding study (i.e. non-detects) are shown in parenthesis. The percentage numbers reflect the fractions of reported measurements above the LOQ (i.e., detects) that are within the range of modeled environmental concentrations in the corresponding zones.

	PFOS		*x*FOSAs		*x*FOSEs	
	Number of measurements (of which non-detects)	Detects within modeled range	Number of measurements (of which non-detects)	Detects within modeled range	Number of measurements (of which non-detects)	Detects within modeled range
Zone 1	38 (36)	50%	167 (82)	91%	194 (96)	6%
Zone 2	22 (17)	40%	13 (6)	86%	12 (6)	0%
Zone 3	31 (16)	67%	31 (4)	81%	31 (5)	15%
Zone 4	48 (9)	62%	8 (1)	57%	8 (1)	0%
Zone 5	43 (13)	70%	11 (3)	38%	11 (2)	0%
Zone 6	29 (13)	56%	22 (9)	23%	22 (2)	0%
Zone 7	27 (8)	0%	8 (6)	0%	7 (4)	0%
Zone 8	18 (9)	0%	8 (5)	67%	8 (5)	0%
Zone 9	24 (11)	0%	27 (8)	95%	25 (10)	0%
Zone 10	0 (0)	-	0 (0)	-	0 (0)	-

S5.6. Potential annual generation of waste stocks in landfills

Wastes are identified to be potentially significant contributors of emissions of PFOS and its precursors into the environment. We performed a simplified scenario analysis to investigate the potential ranges of PFOS and its precursors that may have become waste. We define "waste" here as in the following equation:

$$\text{Waste} = Mass_{\text{produced}} - Mass_{\text{released during production}} - Mass_{\text{released during use and disposed}} - Mass_{\text{stockpiles}}$$

$$= Mass_{\text{landfilled}} + Mass_{\text{incinerated}} + Mass_{\text{dumped on open sites}} + Mass_{\text{placed in open burnings}} + Mass_{\text{recycled}}$$

Where we considered $Mass_{\text{incinerated}}$ = total destruction (no emissions); $Mass_{\text{dumped on open sites}}$ = direct emissions into the environment; $Mass_{\text{placed in open burnings}}$ = partial destruction + emissions; and we assumed that $Mass_{\text{stockpiles}}$ = 0 due to a lack of available data.

In our methodology, we used simplified fractions to reflect releases during the use and disposal phase, which covers releases from these disposal methods above with the exception of wastes that are landfilled (i.e., waste stocks) (and partially in regards to recycling) and incinerated (i.e., total destruction). Landfilled wastes may be slowly released over time and contribute to long-term emissions. In our scenario analysis, we followed the emission inventory scenarios introduced previously in Section S3.4 (and in the main publication) where releases during use and disposal were set as being either 10% (lower scenario), 50% (medium scenario), or 100% (higher scenario) of the production volume. In the low scenario, a 10% release during product use and disposal corresponds with 90% of the production volume becoming waste (and in the medium scenario, 50% becomes waste accordingly). To estimate the range of the amount of potentially landfilled wastes, we additionally assumed that a maximum of 80% and minimum of 20% of generated wastes are landfilled (with the remaining fractions being incinerated with no resulting emissions).

Combining these parameters, the lower inventory scenario (i.e., the higher waste scenario) was defined as 90% of products becoming wastes (corresponding to 10% being released during the use & disposal phase), 80% of these wastes being landfilled, and 98.9% of the landfilled wastes being PFOS and its precursors. The medium inventory scenario (i.e. the medium waste scenario) was defined as 50% of products becoming wastes (corresponding to 50% being released during the use & disposal phase), 20% of these wastes being landfilled, and 80% of these landfilled wastes being PFOS and its precursors. (the homologue compositions of POSF-based products are discussed in section S2.1.4).

Figure S10 shows the results of the scenario analysis using the higher and medium waste scenarios. It shows the cumulative estimated amount of landfilled wastes (from both polymeric and non-polymeric POSF-based products) from the year 1958 until 2030.
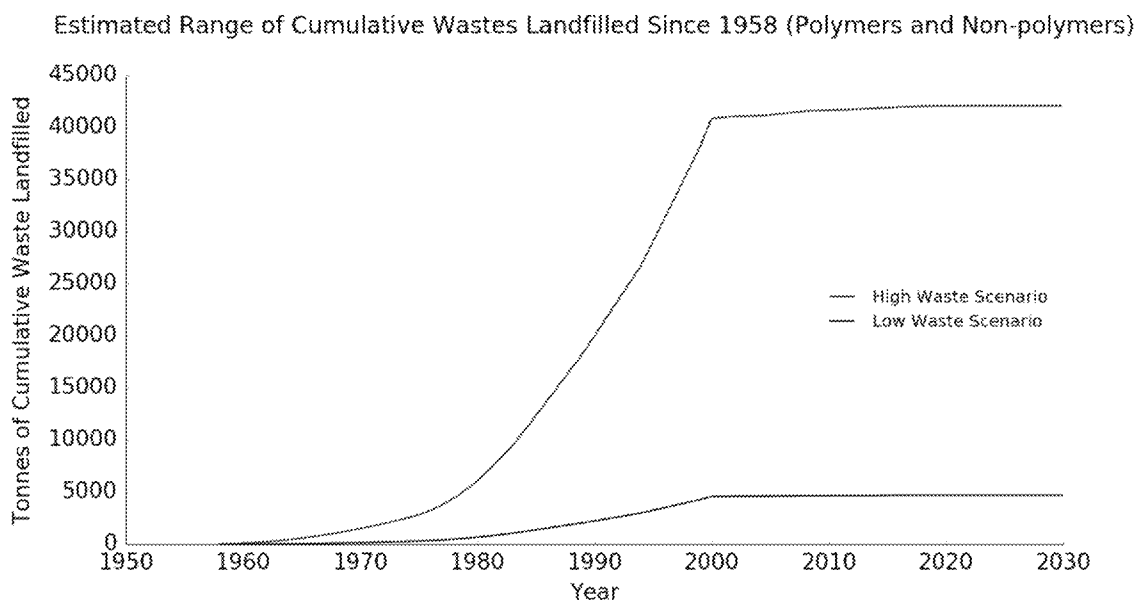
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Estimated Range of Cumulative Wastes Landfilled Since 1958 (Polymers and Non-polymers)

Figure S10: Cumulative estimated high and low scenarios of landfilled POSF-based product wastes since the year 1958 (polymeric and non-polymeric).

S5.7. Degradation of side-chain fluorinated polymers

The degradation of side-chain fluorinated polymers (referred to as polymers) into direct PFOS precursors (i.e., xFOSA/Es) was estimated for various scenarios using our new emission inventory that includes the non-polymeric:polymeric ratios of POSF-based compounds (see section S2.1.3.1). We estimated the potential degradation of both polymers released during use and disposal as well as those in landfills by considering different combinations of potential degradation half-lives and time frames for degradation (the amount of time available for a polymer to degrade).

The degradation of polymers during the use and disposal phase was calculated using hypothetical scenarios: Polymers were assumed to be released over the fixed product lifetime of ten years (evenly distributed annually over the ten years). Once polymers were released into the environment, they were subject to degradation. The degradation was calculated by assuming an unlimited time frame available for degradation ('unlimited' was simplified in the analysis as being 500 years) in combination with hypothetical degradation half-lives (10, 20, 50, or 100 years).

Polymers that are not released during the use & disposal phase end up as waste. We applied a ten-year product lifetime and assumed that all polymers not released during use and disposal phase become waste ten years after they are produced. We used the higher and medium waste scenarios to estimate the amounts of potentially landfilled polymers (see Section S5.6 above). The degradations of landfilled polymer wastes were then calculated using combinations of hypothetical degradation half-lives (10, 20, 50, or 100 years) and time frames available for degradation (10, 20, 50, or 100 years). The resulting amounts of degradation during use and disposal and in landfills were then summed for each corresponding emission scenario (i.e. degradation from the 10% fraction of polymers released during use & disposal were summed with the degradation from the remaining 90% fraction of polymers that become waste) and for each matching hypothetical degradation half-life. The result is a set of scenario estimations of the total amounts of xFOSA/Es formed from the degradation of polymers. Figure S11 shows a schematic for these calculations.
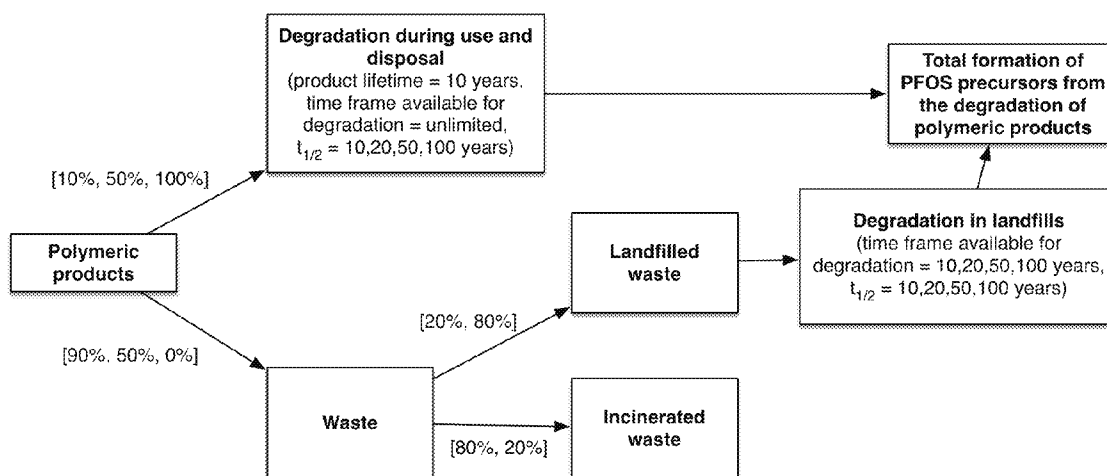
Figure S11: Schematic of the scenario calculations used for the degradation of polymeric products in the use and disposal phase and from landfilled wastes. Mass fractions for each of the scenarios are shown in brackets, and the scenarios for degradation half-life ($t_{1/2}$) and time frame available for degradation are shown in parentheses.

Figure S12 through Figure S15 show the scenario results (varying degradation half-lives and time frames available for degradation) for the lower and medium inventory scenarios (i.e. higher and medium waste scenarios) of the formation of PFOS precursors (xFOSA/Es) from the degradation of polymers during use and disposal and after being landfilled. The total amounts of xFOSA/Es emissions from all other sources in the inventory (see Section S2) are also shown for comparison. However, the formation of xFOSA/Es in landfills from the degradation of polymers does not mean that they may all be released from the landfills immediately. Therefore, this comparison with xFOSA/Es from all other sources should be considered carefully.

While the time frame available for degradation of polymers emitted into the environment during use and disposal cannot be limited, the scenario analysis shows that limiting the time frame for degradation in landfills could influence the overall formation of PFOS precursors.
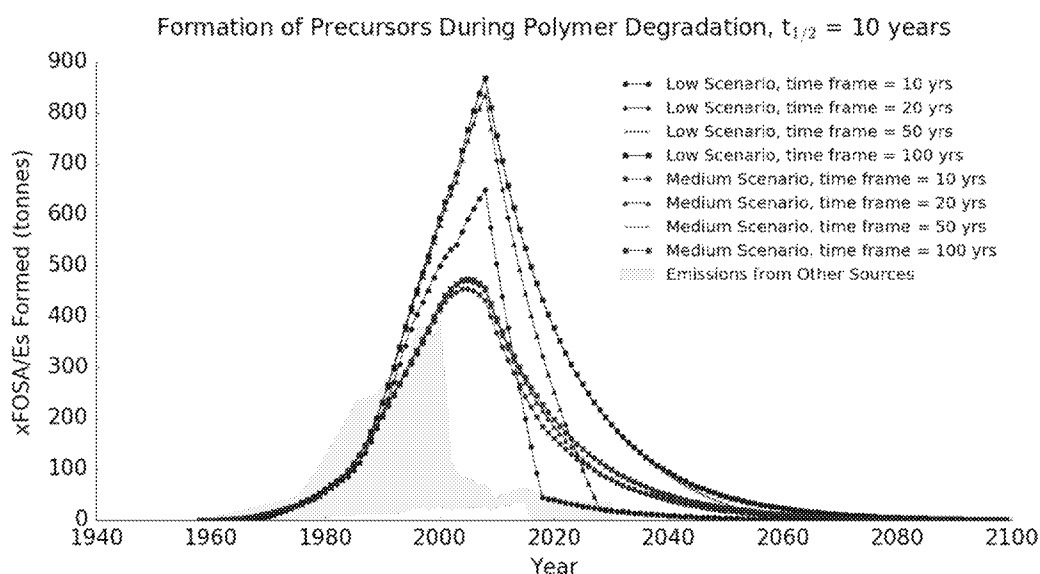
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Figure S12: Estimated formation of xFOSA/Es from the degradation of POSF-based side-chain fluorinated polymers assuming a degradation half-life of 10 years and varying time frames for degradation in landfills for the low (blue lines) and medium (red lines) inventory scenarios. The blue shaded area shows the estimated global annual emissions of xFOSA/Es from all sources except degradation of POSF-based side-chain fluorinated polymers.
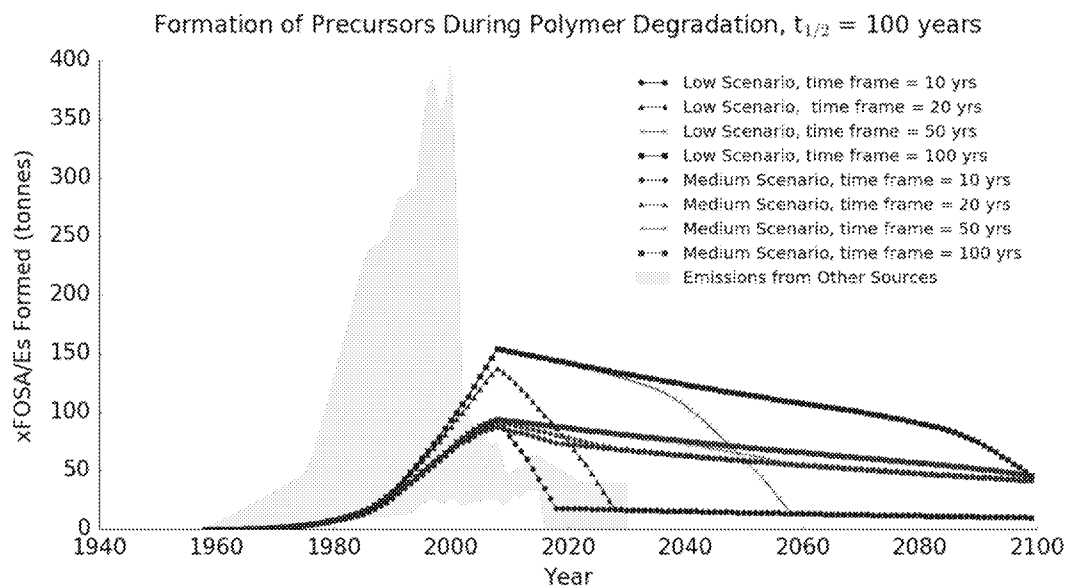

Figure S13: Estimated formation of xFOSA/Es from the degradation of POSF-based side-chain fluorinated polymers assuming a degradation half-life of 100 years and varying time frames for degradation in landfills for the low (blue lines) and medium (red lines) inventory scenarios. The blue shaded area shows the estimated global annual emissions of xFOSA/Es from all sources except degradation of POSF-based side-chain fluorinated polymers.

Formation of Precursors During Polymer Degradation, time frame = 10 years

Figure S14: Estimated formation of xFOSA/Es from the degradation of POSF-based side-chain fluorinated polymers assuming a time frame for degradation of 10 years and varying degradation half-lives for the low (blue lines) and medium (red lines) inventory scenarios. The blue shaded area shows the estimated global annual emissions of xFOSA/Es from all sources except degradation of POSF-based side-chain fluorinated polymers.
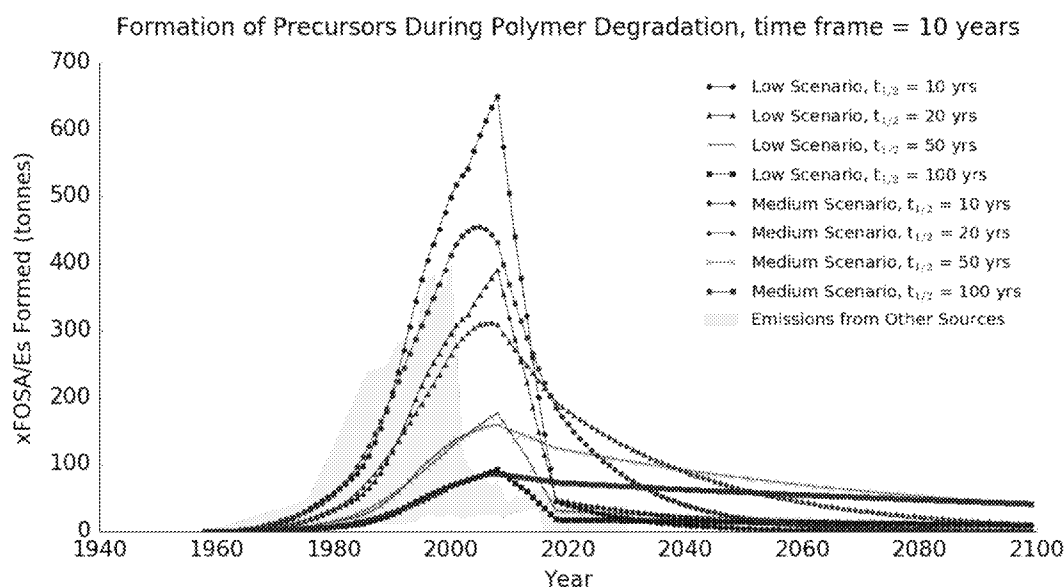

Formation of Precursors During Polymer Degradation, time frame = 100 years

Figure S15: Estimated formation of xFOSA/Es from the degradation of POSF-based side-chain fluorinated polymers assuming a time frame for degradation of 100 years in landfills and varying degradation half-lives for the low (blue lines) and medium (red lines) inventory scenarios. The blue shaded area shows the estimated global annual emissions of xFOSA/Es from all sources except degradation of POSF-based side-chain fluorinated polymers.
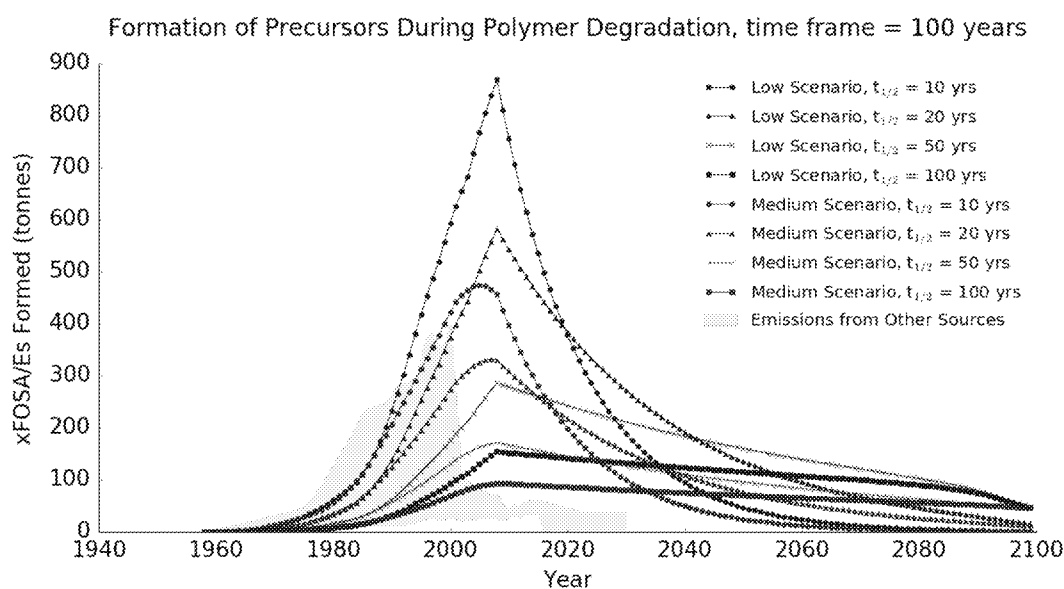
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S5.8. Review and uncertainty scores of individual parameters

As there are different levels of uncertainties attributed to the various source categories, we introduced a scoring system to indicate the level of uncertainty of the parameters considered (see Table S23): 0 to 1 represents low uncertainty (reported estimates and/or measured emissions which have been evaluated for their accuracy); 1 to 2 represents medium uncertainty (expert estimates or measured emissions which have not been (fully) evaluated); 2 to 3 represents high uncertainty (crude estimates or extrapolated emissions).

Table S23: Origin of parameters used in this work to estimate PFSA emissions from POSF-based products. @ = at; ASMP = assumption; CGI = Japan, Western Europe and the United States; Deg = degradation; Emis = emissions; Extrapol = extrapolation; Fig = Figure; Inconc = inconclusive; Interpol = interpolation; MFG = manufacturing; Prod = production; RPT = reports; SI = Supporting Information; Tab = Table; (↑) = overestimation; (↓) = underestimation; (↕) = inconclusive. Uncertainty score A/B = uncertainty level in 1995–2002/uncertainty level in 2003–2015.

QUANTIFICATION STEP	PARAMETERS	1951–2002	2003–2030	UNCERTAINTY SCORES	LOCATION IN THIS DOCUMENT
STEP 1.1 PROD VOLUME	Prod volume in CGI	Company's RPT	OECD RPT + ASMP	0.5/1.0	Table S2, Table S3
	Prod volume in China	Not applicable	UNEP RPT + articles + Extrapol + ASMP	-/1.0	Table S3
STEP 1.2 EMIS @ MFG	Emission factors in CGI	Company's mass flow studies (↓)	Company's reduction RPT (↓)	1.5/1.5	Table S4, Table S5
	Emission factors in China	Not applicable	ASMP: same as before 1998 in CGI (↕)	2.5/2.5	Table S4, Table S5
STEP 1.3 EMIS @ USE & DISPOSAL	Average lifetime of non-polymeric products	ASMP: 2 years	ASMP: 2 years	2.0/2.0	Section S2.1.3.2
	Average lifetime of polymeric products	ASMP: 10 years	ASMP: 10 years	2.0/2.0	Section S2.1.3.2
	Non-polymeric:polymeric ratio in CGI	Company's RPT + Extrapol	OECD RPT+ ASMP: all PFOS	2.0/1.0	Table S6, Table S7
	Non-polymeric:polymeric ratio in China	Not applicable	UNEP RPT+ articles + Extrapol	-/1.5	Table S6
	Unreacted residual levels in products	Company's RPT + Extrapol	Company's RPT + Extrapol	2.5/2.5	Table S11
	Proportions of PFOS in CGI	Company's RPT + Extrapol	OECD RPT+ ASMP: all PFOS	1.5/1.0	Table S8
	Proportions of PFOS in China	Not applicable	UNEP RPT+ articles + Extrapol	-/1.5	Table S8

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	Emissions of EtFOSA in Brazil	Articles + Extrapol	Articles	1.5/1.5	Table S10
	Emissions factors of PFOS in products to water	ASMP: 10-100%	ASMP: 10-100%	3.0/3.0	Section S2.1.3.5
STEP 2. EMIS OF PFSA IMPURITIES	PFCA impurity levels in products	Articles + Extrapol (↕)	Articles + Extrapol (↕)	2.5/2.5	Table S9
	Emission factors of PFSA impurities	ASMP: 100%	ASMP: 100%	2.5/2.5	-
STEP 3. EMIS OF PRECURSORS	Emission factors of residuals in non-polymeric products	ASMP: 10-100% (during use & disposal), 90-95% are complex molecules, 2.5-10% of complex degrade into precursors	ASMP: 10-100% (during use & disposal), 90-95% are complex molecules, 2.5-10% of complex degrade into precursors	3.0/3.0	Section S2.1.3.7
	Emission factors of residuals in polymeric products	ASMP: 10-100% to air	ASMP: 10-100% to air	2.5/2.5	-
	Homologue distribution of PFOS-based products	Articles + Extrapol (↕)	Articles + Extrapol (↕)	2.5/2.5	Table S12
	Homologue distribution of xFOSA/E-based products	Articles + Extrapol (↕)	Articles + Extrapol (↕)	2.5/2.5	Table S13
	Deg rate constants and fractions of formation	Articles + Company's RPT	Articles + Company's RPT	2.0/2.0	Table S14, Table S15, Table S17
	Partition coefficients and activation energies	Articles	Articles	2.0/2.0	Table S16

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